Laser Fabrication of Plasmonic Metal Nanoparticles for

Optoelectronic Devices

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Abstract

Metal nanoparticles (MNP) are widely researched for the fabrication of novel low cost and more energy efficient optoelectronic devices. MNPs, which exhibit surface plasmon resonance (SPR), can be incorporated into thin film photovoltaic structures and as well as into substrates for enhancing the Raman spectroscopy performance. Recent demonstration of devices with plasmonic structures has limited utility due to the need for techniques of ordered MNPs for large area fabrication that are not currently available.

This work examines the suitability of laser annealing for the fabrication of metal nanoparticles in large area optoelectronic devices, as well as the potential for tuning their optical properties precisely within the structure. Gold (Au), silver (Ag) and AuAg alloy particles were fabricated with laser annealing and fully characterized. Morphology characterization of the metal nanoparticle films (MNFs) with scanning electron microscopy (SEM) and atomic force microscopy (AFM) revealed the control over the size by adjusting initial film thickness and laser fluence. Optical characterization with UV-VIS spectrometry demonstrated that SPR of MNFs can be tuned by adjusting the alloy composition, the dielectric constant of surrounding medium, and the size distribution. This experimental result was confirmed by simulations. Direct incorporation of large well distributed Au nanoparticles into solar cells demonstrated enhanced performance. Dense MNFs with small particles decreased the photovoltaic efficiency. By contrast, in the case of Raman, small alloy particles with SPR wavelength close to the pump wavelength demonstrated the best enhancement. High resolution metal nanoparticle tracks written by the laser
demonstrated gas sensing with good sensory capability. However, their high resistivity imposes difficulties in measurements.

We conclude that with suitable optimisations the laser annealing technique studied here could be utilised for the fabrication of metal nanoparticles in large area optoelectronics devices. We demonstrate a number of such applications including solar cells and gas sensors and study the effects of metal nanoparticles within these devices in this thesis.
Dedicated to my family
Declaration

This thesis is submitted for the degree of Doctor of Philosophy at the University of Surrey. This thesis and the work to which it refers are a result of my own efforts. Any ideas, data images or text resulting from the work of others (whether published or unpublished) are fully identified as such within the work and attributed to their originator in the text, bibliography or in footnotes. This thesis has not been submitted in whole or in part for any other academic degree or professional qualification.

Michail Beliatis

December 2011
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Publications

- **Michail J. Beliatis**, Simon J. Henley, and S. Ravi P. Silva, "Engineering the plasmon resonance of large area bi-metallic nanoparticle films by laser nanostructuring for chemical sensors” Optics Letters, 2011, 36 (8), 1362-1364, DOI:10.1364/OL.36.001362
- **Michail J. Beliatis**, Simon J. Henley, and S. Ravi P. Silva, “Laser assisted thermographically printed rainbow color plasmonic structures for photonic circuits” To be submitted

Presentations

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<th>Description</th>
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<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>MNP</td>
<td>Metal Nanoparticle</td>
</tr>
<tr>
<td>SERS</td>
<td>Surface Enhanced Raman Spectroscopy</td>
</tr>
<tr>
<td>SPP</td>
<td>Surface Plasmon Polariton</td>
</tr>
<tr>
<td>SPR</td>
<td>Surface Plasmon Resonance</td>
</tr>
<tr>
<td>MNFs</td>
<td>Metal Nanoparticle Films</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed Laser Deposition</td>
</tr>
<tr>
<td>FF</td>
<td>Fill Factor</td>
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<tr>
<td>RS</td>
<td>Raman Signal</td>
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<tr>
<td>RRS</td>
<td>Resonance Raman Signal</td>
</tr>
<tr>
<td>IR</td>
<td>Infra Red</td>
</tr>
<tr>
<td>VIS</td>
<td>Visible</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate)</td>
</tr>
<tr>
<td>P3HT</td>
<td>Poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>PCB BM</td>
<td>Phenyl-c61-butyric acid methyl ester</td>
</tr>
<tr>
<td>BCP</td>
<td>Bathocuproine</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>BHJ</td>
<td>Bulk Hetero-Junction</td>
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<tr>
<td>MPP</td>
<td>Maximum Power Point</td>
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<tr>
<td>RMS</td>
<td>Root Mean Square</td>
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<tr>
<td>Au</td>
<td>Gold</td>
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<tr>
<td>Ag</td>
<td>Silver</td>
</tr>
<tr>
<td>Pd</td>
<td>Palladium</td>
</tr>
<tr>
<td>r</td>
<td>Radius of nanoparticle</td>
</tr>
<tr>
<td>s</td>
<td>Surface area of nanoparticle</td>
</tr>
<tr>
<td>s_d</td>
<td>Particles separation distance</td>
</tr>
<tr>
<td>λ</td>
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<tr>
<td>P</td>
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<tr>
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<tr>
<td>e</td>
<td>Single electron charge</td>
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<tr>
<td>γ</td>
<td>Damping rate</td>
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<tr>
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<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$A$</td>
<td>Active area of photovoltaic device</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Relaxation time of free electron gas</td>
</tr>
<tr>
<td>$\omega_p$</td>
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<td>Effective mass</td>
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<td>$\varepsilon_d$</td>
<td>Relative permittivity of dielectric material</td>
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<tr>
<td>$J$</td>
<td>Current density</td>
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<td>$E$</td>
<td>Electric field</td>
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<tr>
<td>$\sigma$</td>
<td>Conductivity</td>
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<tr>
<td>$\mu$</td>
<td>Mobility</td>
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<tr>
<td>$k$</td>
<td>Momentum of light</td>
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<tr>
<td>$k_{spp}$</td>
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<td>$\lambda_{spp}$</td>
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<tr>
<td>$c$</td>
<td>Speed of light</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angular frequency</td>
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<tr>
<td>$I_0$</td>
<td>Initial light intensity</td>
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<tr>
<td>$\delta_m$</td>
<td>Penetration depth in metal</td>
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<tr>
<td>$\delta_d$</td>
<td>Penetration depth in dielectric material</td>
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<tr>
<td>$\beta$</td>
<td>Propagation constant of surface plasmon polariton</td>
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<tr>
<td>$E_{spr}$</td>
<td>Electric field from SPR at vicinity of particle</td>
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<tr>
<td>$\phi$</td>
<td>Potential at particle’s vicinity</td>
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<tr>
<td>$\rho_m$</td>
<td>Dipole momentum</td>
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<tr>
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<td>Polarization in the metal nanoparticle</td>
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<tr>
<td>$Q_{ext}$</td>
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<td>Temperature</td>
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<tr>
<td>$h$</td>
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$V_d$ Volume of metal islands
$d$ Metal film thickness
$N$ Concentration of charge carriers
$V$ Potential deference across an electronic circuit
$J_{ph}$ Photocurrent density
$J_{rev}$ Reverse saturation current density
$J_{sc}$ Short circuit current density
$V_{oc}$ Open circuit voltage
$R_{sh}$ Shunt resistance
$R_s$ Series resistance
$n_{eff}$ Power conversion efficiency
$A_b$ Absorption
$S_n$ Sensitivity
$S_l$ Selectivity
$S_r$ Response
$E_F$ Energy at Fermi level
$\Lambda_{air}$ Space charge region
$\omega_S$ Frequency shift from stokes scattering
$\omega_{as}$ Frequency shift from anti-stokes scattering
$\omega_L$ Frequency of incoming light
$\omega_M$ Frequency of light after Raman shift
$P_S$ Power of stokes band signal
$P_{SERS}$ Power of SERS signal
$\sigma_{SERS}$ Scattering cross section
$N_m$ Number of molecules
$N_{SERS}$ Number of molecules under plasmons electrical field
$A(\omega)$ Amplification factor at SERS process
$d$ Distance between particle surface and molecule
$\rho_f$ Density of measured film
$t_f$ Thickness of measured film
$\rho_q$ Density of quartz
$v_q$ Velocity of acoustic wave through quartz
$Z$ Acoustic impedance factor
$f_q$ Oscillation frequency of uncoated quartz
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>$f_c$</td>
<td>Oscillation frequency of coated quartz</td>
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<tr>
<td>$R_{sht}$</td>
<td>Sheet resistance</td>
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<tr>
<td>$Q$</td>
<td>Charge</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Resistivity</td>
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1 Introduction

Ever-increasing demands for more computationally powerful processors, more efficient energy consuming devices, as well as lower cost and smaller dimension electronic devices have lead to the evolution of nanotechnology. Metal nanoparticles (NP) are considered an important building block in nanoscience and nanotechnology which has attracted significant interest of scientific and engineering communities. The compelling inherent optical[1, 2], electrical[3-7] and catalytic[8] properties of metal NP allow them to be used in a plethora of applications. Thus giving rise to room for further research on areas involving their fabrication and utilization of their striking properties for new applications. Metal nanoparticles are reported to be used in devices such as thin film solar cells to enhance their power conversion achieved by efficient light management through surface plasmons [9-12]. Furthermore, they are used in surface enhanced Raman spectroscopy (SERS) for chemical detection [13], gas [14] and biological sensors [15], capacitors [16], memories [17], single electron transistors [18], liquid crystal displays [19] and nanomagnets [20].

For successful use of metal nanoparticles in electronic applications precise control of their size, position and tuning of their physical properties is required imposing challenges in the nanofabrication and deposition process of metal NP. This is besides the requirement for sustaining a low cost of production.

Among metal nanoparticle fabrication methods, rapid laser annealing is relatively new [21] with many advantages against other fabrication methods. Laser annealing for NP fabrication can be applied over large areas fast, at relatively low cost and
without producing any hazard substances. In spite of these advantages, the high power laser beams which are used to melt the initial metal films can induce temperatures beyond the limit which the materials in the vicinity can sustain. Furthermore, methods to tailor the physical dimensions and properties such as the surface plasmon resonance of NP are required to be developed in order to allow the laser annealing method to be used for the fabrication of real optoelectronic devices.

Motivations for this project are instigated by the need to examine if rapid laser annealing techniques can be exploited for the fabrication of metal nanoparticles in cutting edge technological applications requiring methods to tailor the dimension, the precise positioning and tuning of their optical properties. Thus, this project is focusing more on the development of proof-of-concept devices and procedures utilizing the rapid laser annealing method rather than state-of-art electronic devices. Recommendations on how to improve further the procedure and device performance for future work are presented for each case study at the conclusion.

Under the context of emerging technologies where laser nanostucturing could be used in the fabrication process, two application areas were selected to be studied.

Energy conversion from the sun with thin film solar cells is a hot topic with significant room for market growth in order to meet the energy demands of humanity at low cost and minimum atmospheric pollution emissions. Secondly, low cost sensing applications with improved detection at low levels and multi-element detection capabilities are constantly on demand for better metrology and biomedical applications as it is stated in the European road map (Figure 1-1) of photonics and nanotechnology research [22].
Figure 1-1 Market growth and size for technological application of nanotechnology and photonics, reproduced from [22].

One’s sense of wellbeing, in highly developed countries, requires the ability to produce and consume large amounts of energy to fulfill life’s daily work demands. A large proportion of energy demand is considered to be electrical. In order to maintain the good operation levels, low cost and environmentally friendly electrical generation must be maintained. Energy from converting the sun’s radiation to electricity through solar cells is considered one of the most environmentally friendly energy sources. However, the manufacturing cost of solar cells is still relatively high. Thus to lower the cost of solar cells, new technologies which allow facile fabrication, with thinner film cells, are required.

A direct consequence of using thinner active films is the decrease in the quantity of light absorbed within a solar cell which infers lower performances. It has been shown that appropriate designed metal nanoparticles at a moiety interface of two materials with different refractive indexes can sustain enhanced forward scattering
of light [23] due to the surface plasmon resonance (SPR) and yield higher power conversion efficiencies [24, 25].

For the ensemble of plasmonic solar cells which have been demonstrated to date, the limited small areas are a result of manufacturing difficulties of the MNFs for mass production. Implicitly, the ability of laser nanostructuring for large areas by rastering them fast, can be used to fabricate tailored metal nanoparticles directly on the front surfaces of thin film photovoltaic devices for improve performance.

Similarly, the fabrication methods used for NP in sensing devices involve challenges in aspects of reproducibility, precise positioning into the device, tune-ability of their optical and electrical properties for maximizing performance and sensitivity of the sensing element.

Surface enhanced Raman spectroscopy (SERS) is considered a very promising future candidate for ultra sensitive label free detection method. SERS utilizes metal nanoparticle films (MNFs) to enhance the Raman signal of the specimen under detection [26, 27]. However, the high cost [28] to produce fine tuned SERS active test substrates acts as a retardant parameter for wide use of this technology. Thus laser annealing could be used to decorate low cost substrates like common microscope glass slides with properly engineered nanoparticles, reducing the cost of this technology and making it widely accessible to society.

Moreover, due to the nature of the laser annealing process, fine patterns with precisely positioned nanoparticles can be fabricated segregating two or more metal films. Properly engineered structures, like interdigitated patterns, can be used to build elements for chemical resistive sensors or low cost electrodes for prototypes.
In this project we demonstrate several methods to control the dimensions, as well as tune the surface plasmon resonance of metal nanoparticles. Furthermore, it is shown experimentally that metal nanoparticles can be incorporated directly in solar cell devices and sensing devices with laser annealing enhancing their performance and sensitivity, respectively.

1.1 Organization of thesis

A review of the metal nanoparticles physical properties emphasizing the optical characteristics induced by the surface plasmon effect is undertaken at Chapter 2. Furthermore, the concept and theory behind the electrical conductivity in metal nanoparticle films is presented.

In Chapter 3, a review of the current most common techniques used to fabricate metal nanoparticles is undertaken presenting the advantages, and disadvantages. An analysis of laser annealing methods for MNF fabrication is undertaken. The chapter continues with a review of two device applications which are using metal nanoparticles.

An expeditious review of the organic materials which are used for the photovoltaic devices and the photovoltaic effect is presented in section 3.13 referring to device application one. Moreover, the device structures and metal nanoparticle topologies which are implicated with plasmonic enhancement in solar cells are elucidated.

At device application two in section 3.14, a review of sensing elements which are using nanoparticles as active building blocks is undertaken. The fundamental working
mechanisms for electrically conducting sensing elements and surface enhanced Raman spectroscopy for label free sensing are discussed.

A rigorous analysis of the experimental techniques which were employed in this project is presented in Chapter 4 with emphasis given on the fabrication of plasmonic solar cells and the metal nanoparticle based sensing elements.

In Chapter 5 experimental results of fabricated NP are presented. It demonstrates how the deposition method for the initial metal film and the different type of substrates influence the size distribution. Furthermore, unprecedented results on tuning the surface plasmon resonance of NPs only by laser engineering the surrounding medium are elucidated. The technique allows creating bespoke multicolor patterns using laser nanostructuring which coalesces many steps in one process.

In Chapter 6 the fabrication and size control of metal nanoparticles on polymer surfaces are presented. These plasmonic active substrates are used to build organic solar cells and investigate the effect of different particles on the device performance.

The use of laser nanopatterning to fabricate very fine narrow paths filled with NPs is demonstrated in Chapter 7. The structures are used as electrically powered sensing elements for detection of humidity vapours and hydrogen gas at different concentration levels. Parts of this chapter are published in [14].

Results from the fabrication of composition controlled alloy metal nanoparticles to engineer the surface plasmon resonance wavelength are presented at chapter 8. Furthermore the chapter elaborates the intimate relationship of the SPR position with the more efficient coupling of light in organic molecules to enhance their
Raman signal based on experimental results. Parts of this chapter are published in [13].

A summary of the whole project and propositions for improvements and future work are discussed at Chapter 9.
2 Physical properties of metal nanoparticle films

Metal nanoparticles with a diameter smaller than light’s wavelength \( r \ll \lambda \) are known to exhibit peculiar optical and electrical properties. For film structures made of metal nanoparticles their physical properties such as conductivity, light absorption, scattering and wave-guiding are related directly to the size and shape of particles as well as their space separation.

2.1 The surface plasmon polariton dispersion in metals

Free electrons in the conduction band of metals are responsible for their special properties such as good electrical conductivity and light reflectivity. Free electrons under the influence of an electric field move in the direction of the electric field. Considering light as an electromagnetic wave, its electric component influences the movement of free electrons in metals, inducing a displacement. The displacement \( x \) of conduction electrons with respect to positive ion cores cause a macroscopic polarization \( P=-nex \) which is related with the density of free electrons \( n \) and the single electron charge \( e \). Thereafter the electrons motion from the induced electric polarisation is damped via collisions with a characteristic frequency \( \gamma=1/\tau \), where \( \tau \) is in the order of \( 10^{-14} \) sec for ambient temperature and is the relaxation time of a free electron gas [1]. That intimate relationship between polarization from electron motion and collisions damping, causes a collective oscillation of free electrons. Those collective oscillations of a free electron gas are called plasmons – polaritons. For bulk metals the plasma frequency \( \omega_p \) of free electron gas is related with the
density of free electrons \( n_e \), their effective mass \( m \) and the relative permittivity of free space \( \varepsilon_0 \) according to equation[29]

\[
\omega_p = \frac{n e^2}{\varepsilon_0 m}
\]

Equation 2-1

Both the internal current density \( J \) from electron motion and the electric field \( E \) define the conductivity \( \sigma \) as \( J = \sigma E \). Conductivity is in general a complex function of angular frequency \( \omega \) describing the contribution of free electrons to the internal current flow.

The dielectric constant of a metal is expressed as a complex function with dependence on frequency \( \varepsilon_m = \varepsilon_{m1}(\omega) + i \varepsilon_{m2}(\omega) \), representing the response of the free electron gas to a driving electric field.

The Drude model implies that relative permeability is frequency dependent and is given by Equation 2-2[1, 29, 30]

\[
\varepsilon(\omega) = \varepsilon_{int} - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}
\]

Equation 2-2

where \( \varepsilon_{int} \) is a contribution due to interband transitions and \( \gamma \) the total dumping rate which is associated with the mean relaxation time of conduction electrons.

Equation 2-2 indicates that for light frequencies below the plasma frequency \( \omega < \omega_p \) light can influence the movement of free electrons. Therefore propagation of transverse electromagnetic waves in the plasma is not allowed. For \( \omega \geq \omega_p \) the electric component of light is oscillating faster than the electrons. Thus electrons in the conduction band cannot follow the frequency of light due to their momentum inertia leading to negligible damping at free electron plasma thus transparency.
Experimentally relative permeability $\varepsilon_m$ can be deduced by measuring the refractive index $n$ of material with ellipsometry and using equation 4 in reference [1].

$$n^2 = \varepsilon_m = \frac{\varepsilon_{m1}}{2} + \frac{1}{2} \sqrt{\varepsilon_{m1}^2 + (2nk)^2} \tag{Equation 2-3}$$

Where $k=\varepsilon_m/2n$ is the extinction coefficient, expressing the absorption of light by the medium. Hence the imaginary part contributes to the light absorption while the real part is responsible for the polarization. Beer’s law $I(x)=I_0e^{-\alpha x}$ is related with $k$ and for low frequencies implies that the impinging electromagnetic field penetrates inside metal to a particular depth[1]. The penetration depth of the excited surface plasmon polariton (SPP) inside metal is called skin depth[1]

$$\delta_m = \frac{2}{\alpha} = \frac{c}{k\omega} = \frac{2}{\sigma_0\omega\mu_0} \tag{Equation 2-4}$$

Where $c$ is the speed of light, $\sigma_0=(ne^2\tau)/m$ and $\mu_0$ is the DC conductivity and mobility, respectively. A more in depth explanation of the penetration depth $\delta_m$ is further elucidated at chapter 2.3.

![Figure 2-1 Penetration depth $\delta_m$ of surface plasmon polariton into the silver metal. Reproduced from [30]](image-url)
2.2 Excitation of surface plasmon polaritons

The variation of the wavevector $k_0$ (momentum) for light in free space with the angular frequency $\omega$ and speed of light $c$ can be derived from $k_0 = \omega/c$ [30]. In a medium with refractive index $n$ the wavevector of transverse photons is $k = nk_0$ [30], substituting $n$ from Equation 2-3 it becomes

$$k = \sqrt{n}k_0$$ \hspace{1cm} \text{Equation 2-5}

This equation indicates that velocity of light in a medium with refractive index $n$ is always different from the speed of light dispersed in free space.

![Figure 2-2](image-url)

**Figure 2-2** a) Excitation of surface plasmon polariton in a metal-dielectric boundary and b) the dispersion curve of surface plasmon showing the momentum mismatch into dielectric and metal. Reproduced from [31]. The upper and lower curve branches in b) indicate the real and imaginary parts respectively of the complex propagation vector along the SPP propagation axis on the metal-dielectric waveguide structure as a function of the angular frequency $\omega$ [32]. The dashed diagonal line represents the light line in the dielectric medium [33].

The importance of Equation 2-5 lies in the excitation mechanism of SPP's in bulk metallic surfaces, where in order to overcome this momentum mismatch a prism [34-36] or Bragg grating [37] has to be introduced at the metal/dielectric interface to
excite the surface plasmons polaritons. Utilizing a prism, a small angle is introduced in the impinging electromagnetic wave so that momentum at dielectric side is \( k_0 \sin \theta \). At a particular angle or wavelength, in plane momentum at both sites are equal exciting successfully SPPs. In general the propagation constant \( \theta \) of SPP is larger compared to in plane wavevector prohibiting plasmon excitation[1]. Using slabs-pellets with constant distribution length \( x \) on metal surface, phase mismatch occurs when the condition \( \theta = k_0 \sin \theta + \nu g \) is fulfilled, where \( g = 2\pi/x \) is the reciprocal vector of the grating and \( \nu = 1, 2, 3 \). This phase variation equates wavevectors at reciprocal surfaces inducing SPP excitation.

### 2.3 Surface plasmon polariton propagation lengths

For a metal-dielectric structure Equation 2-5 imposes that the wavevector of surface Plasmon \( (k_{spp}) \) is always greater than the wavevector of light in dielectric \( (k_0) \) for the same frequency[1, 30]. The consequence of this mismatch is the small propagation distance of SPP modes away from the surface, following an exponential decay where the energy is dissipated as heat[30]. It has been demonstrated that the momentum of SPP for impinging light perpendicular to the metal plane can be derived solving Maxwell’s equations for specific boundary conditions[31]

\[
k_{spp} = k_0 \sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}} = \frac{\omega}{c} \sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}} \tag{Equation 2-6}
\]

Where \( \varepsilon_d \) is the relative permittivity of dielectric medium and is \( \varepsilon_m \) the relative permittivity of metal. Because SPP rise between two reciprocal interfaces where the dielectric material has a positive real \( \varepsilon_d \) this means that \( \varepsilon_m \) has to be negative and
real[29]. The dispersion relation of SPP is of immense value because further exploitation can give the SPP’s wavelength $\lambda_{spp}$, propagation length $\delta_{spp}$ and penetration length in metals $\delta_m$ and dielectric $\delta_d$.

The dielectric constant of a metal $\varepsilon_m$ is complex thus the SPP momentum has a real and imaginary part given by the following equations[30]

$$k_{spp1} = k_0 \sqrt{\frac{\varepsilon_{m1}\varepsilon_d}{\varepsilon_{m1} + \varepsilon_d}}$$

Equation 2-7

$$k_{spp2} = k_0 \frac{\varepsilon_{m2}}{2(\varepsilon_{m1})^2} \left(\frac{\varepsilon_{m1}\varepsilon_d}{\varepsilon_{m1} + \varepsilon_d}\right)^{\frac{2}{3}}$$

Equation 2-8

Where $k_{spp1}$ and $k_{spp2}$ the real and imaginary part respectively.

SPP wavelength can be derived from the real part of surface plasmon polariton dispersion relation $\lambda_{spp}=2\pi/k_{spp1}$, furthermore for light in free space its wavevector is given by $k_0=2\pi/\lambda_0$ hence substituting to Equation 2-7 the SPP wavelength can be deduced from the following equation[30]

$$\lambda_{spp} = \lambda_0 \sqrt{\frac{\varepsilon_{m1} + \varepsilon_d}{\varepsilon_{m1}\varepsilon_d}}$$

Equation 2-9

Similarly the distance to which the SPP can propagate in plane before the initial power decays is associated with the imaginary part of the dispersion relation, $\delta_{spp}=1/2 \ k_{spp2}$ and can be derived by[29]

$$\delta_{spp} = \lambda_0 \frac{(\varepsilon_{m1})^2}{2\pi\varepsilon_{m2}} \left(\frac{\varepsilon_{m1} + \varepsilon_d}{\varepsilon_{m1}\varepsilon_d}\right)^{\frac{2}{3}}$$

Equation 2-10

As the imaginary part of the metal’s dielectric function is in the denominator, the propagation length increases for metals with low imaginary part $\varepsilon_{m2}$ and high real part $\varepsilon_{m1}$ respectively[29].
If SPP conceived as a wave propagating in three dimensional space and \( z \) is the direction perpendicular to materials boundary plane where propagation is sustained, then from Equation 2-5 the wavevector for \( z \) direction can be written as[30]

\[
k_z^2 = \varepsilon k_0^2 - k_{spp}^2
\]  

**Equation 2-11**

As noted before the surface Plasmon polaritons wavevector \( k_{spp} \) is always higher than \( k_0 \), which imposes that the SPP wavevector at \( z \) direction is imaginary for both media. This yields an exponential decay of field in both dielectric and metallic materials. Hence substituting Equation 2-11 into Equation 2-6 penetration depths \( \delta_m \) and \( \delta_d \) are derived from the following equations[30] assuming that \(|\varepsilon_{m1}| \gg |\varepsilon_{m2}|\).

\[
\delta_m = \frac{1}{k_0} \left| \frac{\varepsilon_{m1} + \varepsilon_d}{\varepsilon_d^2} \right|^{\frac{1}{2}}
\]  

**Equation 2-12**

\[
\delta_d = \frac{1}{k_0} \left| \frac{\varepsilon_{m1} + \varepsilon_d}{\varepsilon_m^2} \right|^{\frac{1}{2}}
\]  

**Equation 2-13**

Relative permittivity varies as a function of frequency therefore one can speculate that penetration depths are frequency dependant, an important asset for designing devices where the field interacts with matter such as in surface enhanced Raman spectroscopy, and polymer thin film solar cells.

An indication of the different length scales induced at visible and infrared light wavelengths is displayed at Figure 2-3.
2.4 Localized surface plasmons

Metal nanoparticles with diameter much smaller than wavelength of light $d<<\lambda$ exhibit localised surface plasmons which unlike with SPPs in bulk metals are non-propagating excitations. The small size of nanoparticles imposes a high density of free electrons in their curved surface, which couple strongly to the impinging electromagnetic field avoiding the necessity for extra mechanism to overcome momentum mismatch problems [1]. The displacement of those electrons in the field results in strong restoring forces, leading to a collective resonance oscillation. This resonance induces amplification in the electric field in the vicinity of particles and is called surface plasmon resonance (SPR)[1, 2, 31].

Reproduced from [30].
For nanoparticles with dimensions below 100nm the electromagnetic field of light can be considered as constant over the particle volume hence the quasi-static model can be used for analysis. The potential in the vicinity of particles can be calculated using the following equation[1].

\[
\Phi = -E_0 r \cos \theta + \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d} E_0 s^3 \frac{\cos \theta}{r^2}
\]

Equation 2-14

\( \Phi \) describes the potential which arises from the dipole located at the particle’s centre. \( s \) and \( r \) are the surface area and radius of particle, respectively \( \varepsilon_m \) is the dielectric constant of the metal nanoparticle and \( \varepsilon_d \) is the relative permittivity of the surrounding dielectric. Thus the electric field in the vicinity of particles can be expressed as \( E = -\nabla \Phi \). Introducing the dipole momentum \( \rho_m = \varepsilon_0 \varepsilon_d \alpha E_0 \) in Equation 2-14 it has been demonstrated that the polarization \( \alpha \) in the particle can be deduced[2]
Polarization reaches a maximum when the denominator in Equation 2-15 is close to zero. This requirement implies that the resonance of collective oscillations occurs when the real part of metal dielectric is equal to

\[ Re[\varepsilon_m(\omega)] = -2\varepsilon_d \]  

Equation 2-16

This equation is known as Frohlich condition. For spherical shaped metallic particles in air, the Drude model Frohlich condition is fulfilled for \( \omega_0 = \omega_p/\sqrt{3} \) [1].

The resonance frequency (SPR) dictates the colour of metal nanoparticle films. On the basis of Equation 2-15, relative permittivity from both dielectric and metallic materials are strongly influence that local resonance frequency. Furthermore due to the surface area parameter \( s \), different size and shape particles yield different intriguing coloured metal nanoparticle films.

The polarization \( \alpha \) at surface of metal nanoparticles enhances the electric field in the vicinity. Furthermore it is responsible for enhancing the efficiency of scattering (Equation 2-18) or absorption (Equation 2-19) of light which occurs on metal nanoparticles. Due to the intimate relation, the overall effect on light is expressed as the sum of both[39] \( Q_{\text{ext}} = Q_{\text{sca}} + Q_{\text{abs}} \), known as the extinction coefficient (Figure 2-5).
Figure 2-5 Theoretical estimation of extinction, scattering and absorption coefficients for a 20nm diameter Au particle in vacuum, across visible and near-infrared wavelengths.

It has been demonstrated that all components can be calculated numerically from the following equations [1, 40, 41].

\[
Q_{\text{ext}} = \frac{9}{8\pi} \frac{\omega^4 \varepsilon_d^{3/2} V}{c} \left( \frac{\varepsilon_m^{(im)}}{\varepsilon_m^{(re)} + 2\varepsilon_d} \right)^2 + \varepsilon_m^{(im)} \quad \text{Equation 2-17}
\]

\[
Q_{\text{sca}} = \frac{k^4}{6\pi} |\alpha|^2 = \frac{8\pi}{3} \kappa^4 s^6 \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d} \quad \text{Equation 2-18}
\]

\[
Q_{\text{abs}} = k l m |\alpha| = 4\pi k^2 s^3 l \left( \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d} \right) \quad \text{Equation 2-19}
\]

These parameters are of immense value in the design of active optical devices where the light can be waveguided and confined at sub-wavelength dimensions[31].

The term \(s^6\) in Equation 2-18 indicates that scattering is increasing tremendously with volume [41, 42]. Moreover the involvement of polarization factor leads to red
shift of SPR as the particle’s dimension increase, although that shift is smaller compared to the red shift resulting from increase in the relative permittivity of the surrounding medium [1, 39]. So far scattering and absorption have been considered only for a single particle, however for an MNF a crucial factor which influences these factors is the coverage of the film. For small interparticle distances, particles can be considered as interacting dipoles where the total electric field is the superposition of all individual neighbouring fields leading to strong field enhancement, increased absorption and SPR shift [41, 43]. Hence interparticle distance and particles size has to be carefully designed to acquire the desired effect for surface enhanced Raman spectroscopy, where a closely packed array is more suitable due to high electric field enhancement. On the other hand big particles widely separated are more favourable for applications where forward scattering is required, such as solar cells.

2.5 Electrical conductivity in metal nanoparticle films

The conductivity mechanism at metal nanoparticle films can vary significantly as a function of large number of parameters. Inter-particle distance, size of particles, number of layers, the surrounding dielectric medium and the percolation level of particles into a film are the main influential parameters for electron flow in MNFs. In general, conductivity can be distinguished in two categories on the basis of density of particles in the film. For ensembles where particle density exceeds the percolation level, the particles are attached forming a low resistivity electrical path which is amenable by Ohm’s law. The second category is for MNFs with particles concentration well below the percolation level. For such kind of films where in
addition to low concentration levels the separation distance between particles are <5nm, intriguing electrical properties are observed [5, 44, 45].

Although in such films metal particles are clearly separated by a gap filled with dielectric material, they exhibit current flow. It has been proposed that this type of electron transportation in such type of MNF’s is caused be electron tunnelling between nanoparticles, which are followed by mechanical vibrations[5].

Applying potential between two close-distanced, separated, electrodes which are filled with metal nanospheres constrains them to get charged. This charge in metal nanoparticles induces a strong electrostatic field between them. The Coulomb forces among the charged nanospheres enables electron transportation due to electron tunnelling[46].

The capacitance for a sphere is given by formula

$$C_0 = 4\pi\varepsilon_d\varepsilon_0 r$$  \hspace{1cm} \text{Equation 2-20}

If $V_{L(R)}$ are the voltages and $X_{L(R)}$ the positions at Left and Right electrodes, respectively then the electric field between these electrodes is

$$E = -\frac{V_R - V_L}{(X_R - X_L)}$$  \hspace{1cm} \text{Equation 2-21}

At room temperature the activation energy $E_a$ for the initiation of the tunnelling effect is given by Equation 2-22 [47, 48]

$$E_a = \frac{e^2}{4\pi\varepsilon_d\varepsilon_0} \left( \frac{1}{r} - \frac{1}{r + s_d} \right)$$  \hspace{1cm} \text{Equation 2-22}
Where $\varepsilon_d$ and $\varepsilon_0$ are the dielectric constants of medium between spheres and vacuum respectively, $r$ the particle’s radius, $e$ the particle’s charge, and $s_d$ the spacing between the surface of two particles.

Two conditions have to be fulfilled for a successful single electron tunnelling to occur. The charging energy $E_c$ from adding an electron to a metal nanoparticle with capacitance $C_0$ has to be bigger than the thermal energy $E_T$ [18].

$$E_c > E_T \iff \frac{e^2}{2C_0} > k_B T$$ \hspace{1cm} \text{Equation 2-23}$$

where $k_B$ is the Boltzmann constant and $T$ the temperature of the systems.

Second, the tunnelling resistance from electrodes to metal islands has to be larger than the quantum resistance, defined as $h/4e^2(=6.5\text{K}\Omega)$ with $h$ representing the Planck constant, to minimise the fluctuations of charge[18].

Concomitantly the conductivity $\sigma$ for such a MNF can be modelled according to the following equation [44, 49-52]

$$\sigma = e^{-s\phi} e^{-E_0/k_B T}$$ \hspace{1cm} \text{Equation 2-24}$$

where $\phi$ is the electronic coupling coefficient between metal nanoparticles.

In general a nanoparticle can be modelled like a capacitor in parallel with a resistance representing the capacitance and conductance of the particle [7, 18].

Au and Ag nanoparticles covered by Teflon or nylon to create a known dielectric material around the metal particles has been previously studied [3]. The electrical properties of such structures depend on the metal filling factor and the array structure. Increasing the metal filling factor equates to bigger particles where after a certain level percolation dominates creating a ohmic conductive path[3]. However
conduction in a metal-dielectric structure like that can be the result of electron hopping between defects in the insulating material as opposed to electron tunnelling. The exact mechanism of transportation in such films is a trade between the size of particles, the inter-particle distance and the dielectric material[8].

The study of the electrical behaviour of such metal nanoparticle films by several groups has shown that they can used to fabricate very sensitive and relatively low cost sensors with well defined electrical characteristics [8, 14, 53].
3 Literature review of metal nanoparticle fabrication and device applications

There is an abundance of techniques to fabricate metal nanoparticles, however each method has advantages and disadvantages, imposing limitations on their applicability for use in specific applications. A brief survey in the context of metal nanoparticle (MN) fabrication methods is undertaken, investigating the most common MN fabrication methods. Their advantages and disadvantages are compared in terms of limitations imposed in the production of particles for large area electronics.

3.1 Chemical reduction

A facile method to synthesize metal nanoparticles is chemical reduction in liquid phase. The metal compounds are represented by their salts, such as borohydrides which are mixed with a chemical reducer for decomposing the initial solution and releasing the metal element to form nanoparticles. This method is popular for its simplicity but requires vast amounts of chemical solutions, producing significant amount of hazardous wastes. For synthesis of Ag colloids mixing a solution of AgNO₃ with trisodium citrate is reported to form 10-15nm particles [54, 55]. Similarly, for Au colloids HAuCl₄ is diluted in distilled water and blended with trisodium citrate[54, 55] resulting in 40-50nm gold spheres. In general the particles’ size is controlled by adjusting the concentration of chemicals in the solution.
3.2 Photo reduction

An alternative method to reduce AgNO₃ thus synthesize metallic grains is the use of photo reduction. Instead of mixing chemical solutions the AgNO₃ solution is irradiated with high power UV light to break the chemical bonds and release the Ag element enabling grain composition. Typically the solution is irradiated with 25ns pulse duration from an excimer laser at 248nm wavelength and fluence 224mJ/cm² for approximately 10 minutes. The solution has to be irradiated uniformly all over its volume to ensure uniform reduction[56]. Ag particles with diameter 50 to 500nm are reported to be fabricated. Although this method reduces the necessity of multiple chemicals, the drawback is the wide distribution of diameter size as well as the cleaning process of the remaining chemical which produces a big amount of hazardous wastes, furthermore additive chemicals such as sodium citrate or sodium dodecylsulfate [57] required to prevent aggregation of metal nanoparticles.

3.3 Thermal annealing

Thermal annealing for metal nanoparticles fabrication is widely used in optoelectronics. It is based on annealing very thin metal films deposited on a smooth thick ceramic substrate typically at 300 - 500 °C for a few hours in vacuum or N₂ filled chamber. The initial metal film thickness is typically a few nanometers: 2-100nm. Uniform size spherical particles are reported to be produced with this method[9, 58, 59] The size, shape and separation distances of particles are strongly influenced by annealing temperature, duration, initial film thickness, and reaction of the metal
with the substrate [59]. Disadvantages of that process are the slow processing as well as the finite area of annealing chamber.

3.4 Evaporation

Evaporation of thin metal films at low rates $0.2\,\text{Å/s}$ can form small grains on glass substrates. For successful fabrication, the evaporation must be performed under very low vacuum typically $5\times10^{-8}\,\text{Torr}$. This requirement for deep vacuum levels is mainly limiting the wide use of that technique. It has been shown that islands with average diameter of $10.5\,\text{nm}$ can successfully formed [58, 60].

3.5 Ion implantation

Particles within sapphire or silicon/SiO$_2$ can be fabricated using ion implantation. Advantages of this method are high filling metal factor in the irradiated area and the ability to create nanoparticles at different depths. Generally the formation mechanism can be divided in four steps: First, metal atoms penetrate into the sample; Second, saturation of metal atoms in the area under the spot; Third, formation of nuclei constituted from several metal atoms; and finally formation of nanoparticles. The size of nanoparticles is controlled by altering the ion concentration profile and current density[61]. This method requires multiple steps and is difficult to control. Moreover, it is difficult to apply this technique on flexible substrates.
3.6 Electron beam and Ion beam lithography

Electron beam lithography is a method which yields excellent precision in the fabrication of nanoparticles and nanopatterns as well as very good reproducibility [62]. A beam of electrons is used to etch a thin film deposited on the substrate’s surface creating the desired patterns. Eliminating the use of mask thus, diffraction limits of light high resolution nanoscale structures can be fabricated. Similarly ion beam lithography uses a beam of accelerated ions for the etching[63]. The very long time to expose areas above 1 cm² is the main limitation for both techniques.

3.7 Nanosphere lithography

A truly innovative and relatively facile method is the coating of the substrate with a dense monolayer of small polymer nanospheres forming a shadow mask. Between the boundaries of attached spherical particles small holes are formed. Deposition of a thin metal film using sputtering or evaporation is performed thereafter to fill those holes. Finally the substrate is immersed into a solvent solution to dissolve the polymer spheres and leave the remaining metal nanoparticles. Advantages of this technique are the well defined particles with constant size and periodic patterns in addition with the ability to create different shapes rather than simple spherical nanoparticles Figure 3-1. The size of particles is controlled utilizing polymer spheres with appropriate diameter and controlling the deposited thickness of metal. With a monolayer of polymer spheres, fabrication of triangle Ag nanoparticles with diameter in the range of 21 to 126nm and height 4 to 46nm has been demonstrated
Nevertheless, the dissolving process requires a number of chemical solutions productising hazard wastes which is the main disadvantage of that method.

![Diagram of sphere lithography](image)

Figure 3-1 Diagram of sphere lithography a) single layer of nanosphere mask b) the periodic array pattern and c) the actual nanoparticles produced by this method. Reproduced from [65]

### 3.8 Metal oxide mask

Porous metal plates of anodized aluminum oxide can serve as a template mask for evaporation or sputtering. The sputtered or evaporated metal atoms are much smaller than the anodic aluminum oxide pores, concomitantly well structured nanoparticles can be grown on a substrate. Mask fabrication is normally done through anodizing aluminium sheets. Anodization is typically performed at 80V within a solution of 0.3mol/l oxalic acid and 0.3mol/l manolic acid. Varying the applied potential, the size of the pores can controlled. Finally the pores are developed by etching the aluminum sheet in 5% diluted phosphoric acid. Formation of Ag metal islands with diameters of 110nm and 220nm height has been reported [66]. The finite size of chamber where metal film is deposited through the anodized aluminum mask and use of production of chemical waste hazards are the main drawbacks. Furthermore relatively big particles can only be produced with this method.
3.9 Pulse Laser Deposition

Pulse laser deposition (PLD) is a well known fabrication technique for metal nanofilms and nanoparticles. Its advantages are the broad number of different target materials which can be deposited. The laser beam is focused down on the rotating target within a tiny spot typically $1 \times 10^{-4}$ cm$^2$ aiming an effective laser fluence of 1 J/cm$^2$. The substrate is placed exactly in front of the beam spot at a distance around 9cm away and keeping the pressure in the chamber below $5 \times 10^{-5}$ mbar. Evaporation of the target material ensues from each pulsed laser irradiation. It has been demonstrated that Ag and Au particles with striking colors in the visible regime can be synthesized [67, 68]. PLD limitations derive from the size of chamber, the difficulty to define the mass deposition per pulse, and the non uniformity of the deposited grains.

3.10 Liquid phase laser ablation

In liquid phase laser ablation a slab of bulk metal is immersed in a liquid. The laser beam is focused down to 1mm$^2$ to achieve high laser fluencies typically in the range of 1.4MW/mm$^2$. The process can be done using water, however polysiloxane oil is preferred to minimize oxidation and aggregation. The laser heats the bulk metal surface and cause ablation. Particles with sizes of 2-60nm can be fabricated from Ag or Au metal plates [69-71]. Concentration and nanoparticle’s size in the final solution are related with the oil’s molecular weight; the higher the molecular weight the smaller the particle size and concentration. Disadvantages of that method are the
relatively wide range of nanoparticles as well as the difficulty to clean the metal nanoparticles from the liquid oil.

### 3.11 Lifted Induced Forward Transfer

Lifted induced forward transfer (LIFT) is a method to create and deposit simultaneously metal nanoparticles with relatively high precision using a laser beam[72, 73]. A quartz window is normally coated with a thin film ~15nm of the metal from which particles will be formed. The quartz window is placed above the substrate with the metal covered side facing the specimen where the particles are aimed to be deposited. Appropriate pillars are used to create a small gap between quartz and substrate, typically a few µm (Figure 3-2). The structure is irradiated with a laser at 248nm. At this wavelength the quartz window is transparent allowing the energy to be absorbed in the metal film. The high laser fluence causes melting and evaporation of the metal film. The evaporated metal is sprayed on top of the specimen with relatively high accuracy; the collisions of metal’s atoms with atmospheric air cause elimination of wide spread. The main disadvantages are the wide range of particles size and its complexity due to large number of processing steps.
3.12 Rapid Laser thermal annealing

Rapid laser annealing for metal nanoparticles fabrication is a relative new method with lots of advantages. Henley and co-authors first reported it in 2004 as a process to synthesize catalysts for carbon nanotubes' growth[74], although laser annealing itself was commonly used in electronics fabrication for many years. Laser annealing is known to be used for amorphous silicon crystallization for transistors[75] and solar cells[76], electrodes patterning for displays[77] and solar cells[78], at ion implantation to activate the doping[79, 80], metal welding and cutting[81], as well as in preparations of optical filters[82]. Constant development of Laser technology has made it possible to achieve very high delivered energy densities, demonstrating powers up to terawatt[83]. These high power beams can be used for laser treating large areas very fast. In general high power lasers operate in short pulsed mode for higher performances since the laser intensity is inversly proportional to the pulse width. Moreover shorter pulses are more favourable for surface treatments due to
lower damage induced in the underlying substrates. For high power laser beams with a single pulse[84] is possible to yield the desired thermal effect, however it is more common that multiple pulses are applied[85]. Unfortunately the high reflectivity of metals leads to a large amount of wasted energy. Nevertheless the remaining energy of the impinging light is absorbed efficiently within a few nanometers from the surface. The accumulation of heat in the metal surface can lead to deformation. Henley [21] first studied systematically the rapid laser annealing of thin metal films on silicon substrates, where he demonstrated that appropriate laser fluence, can melt the initial film leading to uniform metal nanoparticles formation as illustrated in Figure 3-3.

For high power laser beams, pulsed laser systems with pulse duration in the range of ns – fs are required. These types of lasers, combined with short wavelength light beams, such as in an Excimer laser are ideal for rapid thermal annealing due to their capability of inducing high thermal effects. The method is suitable to be applied on different substrate materials such as plastics or ceramics without damaging them substantially.
Figure 3-3 Graphical representation of metal nanoparticles fabrication using laser annealing.

Rapid laser annealing, due to its unique nature, can be used to fabricate metal nanoparticles very fast over large areas by rastering. On the flip-side decreasing the spot size with appropriate optics the technique is ideal for fabricating accurately metal nanoparticles within very narrow paths. Furthermore the technique does not produce any hazard wastes, which is a big advantage for environmental sustainability.

3.12.1 Phase transformations

Laser annealing of thin metal films below 40nm can be grouped in three regimes based on the amount of irradiated energy and the thermal impact of the energy with matter.

The first regime is observed from laser beams which deliver low energy densities, leading to heat rising at levels below the fusion threshold of the irradiated material.
Hence the temperature on the surface increases but the metal film remains stable in its original solid state.

The second regime is where moderate laser fluencies are delivered on the film. In this regime, the imposed thermal energy exceeds the fusion point of the material while it is still lower than its evaporation threshold. For energy densities in this regime the temperature of the thin metal films increases rapidly until it melts. For substrates which aren’t “wetted” by the metal in the liquid phase, the melted metal coalesces to spherical or semi-spherical shaped particles due to surface tension[21, 86] and solidifies as it cools down.

For high laser fluences, which heat the film above the evaporation point, ablation of the metal film occurs, producing a plume of metal atoms. In this category the pressure of the surrounding medium sustains an important role for the nanoparticle’s formation. It has been shown that for low vacuum pressures, the evaporated material can travel relatively long distances depositing thin films (PLD)[68, 87], while for atmospheric pressures the air forms a barrier causing the metal atoms to be scattered back onto the substrate and aggregate forming metal nanoparticles [14].

### 3.12.2 Nano-particles formation mechanism

Nanosecond pulsed excimer lasers can induce rapidly vast amount of heat at thin metal films leading to metal melting. Henley [21] observed that metal in liquid phase break down to smaller droplets due to surface Rayleigh instability, for substrates which allow metal-substrate interaction without getting “wet” on the specific molten
metal. Under those conditions droplets converge to spherical shaped nanoparticles due to surface tensions.

Figure 3-4 SEM images of laser annealing 20nm thick Au film for producing metal nanoparticles. The fluences used were a) 0 mJ/cm², b) 125 mJ/cm², c) 250 mJ/cm², d) 430 mJ/cm². Reproduced from [21]

The thermal effect is proportional with the pulse width, thus for thin metals films that is implying, short cool down period ~100ns for metal solidification. This very short solidification time prevents the metal nanoparticles from aggregation. It is reported that thicker films 15-40nm require less energy to melt compared to thin films <15nm due to more efficient light energy absorption. The size of nanoparticles and their spatial distribution are related to initial film thickness and roughness of substrate. The initial metal island’s volume $V_d$ can be estimated from the following equation [21]

$$V_d = \frac{4\pi r^3}{3} \propto \frac{L^2 d}{N}$$  

Equation 3-1

where $r$ is the nanoparticle radius, $d$ is the initial metal film thickness, $L$ is the distance between the perforations, and $N$ is the number of liquid droplets produced.
For a metal in liquid phase the diameter of droplets is determined by the Rayleigh instability criterion, hence the final particles radius tends to be proportional to the initial film thickness according to equation[21].

\[ r \propto \sqrt{\eta d} \]  

Equation 3-2

As the temperature increases in the metal some dissipation of the accumulated heat is expected at the surrounding materials. Heat conduction to surroundings is determined by their thermal conductivity. However due to short pulse widths the thermal cycle (heating-cooling) remains very short keeping the heat penetration levels into the surroundings low[21]. This allows the substrate to remain at low macroscopic temperature, favourable for fabricating nanoparticles on temperature sensitive substrates such as plastic.

A slightly different approach for the formation mechanism is proposed by Trice[86], where the metal nanoparticles come from the spinodal dewetting of thin metal films. The inherent intermolecular forces and surface tensions in metal film and substrate are leading to well predicted spinodal dewetting lengths, thus formation of self organized nanoparticles with predictable size and spatial distributions even for bilayer initial metals films can occur [88, 89]. A direct consequence of this concept is the different well defined metallic shapes which are observed when patterned initial films are laser annealed [90].

3.12.3 Effect of laser annealing in bulk material

Laser annealing involves a large amount of heat, which can substantially affect the electrical[76, 80], optical[91, 92] and mechanical[93] properties of matter. Implicitly
the delivered energy is affecting the bulk substrates in a similar manner as with the thin metal films. Different levels of irradiation during laser annealing can enhance or degrade the electric conductivity of materials[91].

3.13 Device application one: Polymer solar cells with metal nanoparticles

The initial discovery in 1977 [94] of conductive organic polymers at room temperatures by doping polyacetylene with iodine established a new research area which gained significant attention in the scientific community over the last decades. In 1985 [95] the first bilayer organic solar cell demonstrated a power conversation efficiency of 1% and in 1987 [96] the first rectification diode made from solution processable materials marked a significant change in the electronics field. Their unique properties of flexibility, easy processing and low fabrication cost makes them ideal candidates for plastic electronic devices, such as light emitting diodes[97], transistors[98] and solar cells[99].

The properties of organic materials can be tailored by molecular design to suit different functionalities (optical absorption, electrical conductivity, mechanical flexibility). One highly important characteristic determined during chemical synthesis in polymers is the extent of conjugation in their chains. An alternating single and double bond structure in the carbon chain of a polymer is called a conjugated chain and gives the polymer its conducting or semiconducting nature. Despite the huge improvements in conjugated polymers synthesis during the last decades the mobility
of electrons in these materials is still very small compared to silicon, implying limitation in the design and fabrication of organic photovoltaic diodes.

### 3.13.1 Conductive polymer material properties

Conductive polymers are based on unsaturated planar carbon chains with an alternation between single and double bonds know as a conjugated carbon chain. In conjugated structures the π orbital electrons can move more easily compared to σ orbital electrons[100]. For example, in the conjugated polymer trans-polyacetylene, only three of the four valence electrons of carbon participate in σ-backbone with one remaining electron which it is located in a π orbital[101]. These π orbital electrons can be conceived as a delocalized electron cloud with a periodic alternating density[101], and they are responsible for light absorption or emission in solar cells and light emitting diodes respectively.

That periodic alternating density of π orbital electron cloud forms two molecular bands, the π band corresponding to the highest occupied molecular orbital (HOMO) and the π* band corresponding to the lowest occupied molecular orbital (LUMO). The existence of those two bands forms an energy gap (Figure 3-5) which for organic semiconductors is related with the electron-phonon coupling and the dimerisation distance[101]. In conjugated polymers with non-degenerated ground state excitons, polaron and bipolaron quasi-particles are able to exist evolving new states within the forbidden bandgap.

Conjugate polymers can be characterised as n-type or p-type depending on their ability to withdraw or accept an electron, respectively. This effect can be conceived
as a type of doping in comparison to inorganic materials. Doping in organics occurs via charge transfer reaction when an element such as oxygen is introduced inducing oxidation or reduction[101]. This reaction leads to a net charge onto the polymer chain which it attributes the characteristic doping-type.

**Figure 3-5** Electron orbital form band $\pi$ corresponding to highest occupied molecular orbital (HOMO) and band $\pi^*$ corresponding to lowest occupied molecular orbital (LUMO).

Excitation of such polymers with appropriate energy photons yield one electron and one hole per chain, which are strongly bound due to strong Coulomb attraction forces which arise between opposite charges[100].

Bipolarons are pertained with double charged carriers having the same polarity. The strong interaction between electron-phonon can induce stabilization of two charges despite the repulsion from Coulomb’s forces[101].
At room temperatures charge transport in this type of polymers is proposed to be thermally activated charge hopping between localised states in adjacent polymer chains (Figure 3-6) [102, 103].

![Diagram](image-url)

**Figure 3-6** Charge transport by hopping between adjacent localized states, reproduced from [103].

In heterojunction solar cells the holes are mostly transported in donor materials while the electrons in acceptor materials[103]. The mobility in these materials is influenced by free carriers density and electric field. Singlet excitons have a lifetime of around one nanosecond while triplet excitons can live up to milliseconds, after that time period, they recombine radiatively [103]. Diffusion lengths for excitons are shown experimentally to be in the range of 3-30nm for conjugated polymers, a value which is much smaller that the optimum length for light absorption[103]. Thus the utilisation of bulk heterojunction principle where two semiconducting materials are blended is it more suitable for charge transportation in organic solar cells. For more details about organic materials properties should refer to [103].
3.13.2 Fundamentals of the photovoltaic principle

The photovoltaic effect involves electrons generation in photoactive materials when photons are absorbed, hence for a closed loop circuit, current flow is observed. Generally for photovoltaic diodes based on inorganic materials such as silicon (Si), amorphous hydrogenated silicon (a-Si:H) and cadmium tellurium (CdTe) free electron-hole pairs are generated throughout the absorbing material. Separation of electron and holes is occurs in the depletion region of the p-n junction due to the internal electric field which drives them through a drift process to electrodes for collection Figure 3-7. In a closed loop electric circuit, that drift current powers the external load.

![Diagram of electron and hole drift in a p-n junction.](image)

**Figure 3-7** Electron – hole extraction in silicon based solar cells due to drift current.

Organic based photovoltaic diodes operate in the same principle but with a fundamental difference. An absorbed photon in polymer, generates a quasi-particle that is considered as a bound electron-hole pair due to strong Coulomb forces which
is usually known as Frenkel exciton or Mott-Wannier exciton if the delocalization extends over many molecular units. Exciton separation occurs via an interfacial exciton dissociation process[101, 103]. The excitons separation is driven by the band offset at the interface of two materials with different band levels of unoccupied molecular orbitals which form a potential difference[103] Figure 3-8.

![Graphical representation of interfacial exciton dissociation process at bulk heterojunction polymer solar cells](image)

**Figure 3-8** Graphical representation of interfacial exciton dissociation process at bulk heterojunction polymer solar cells, reproduced from [103].

If the ionisation takes place in a random place in absence of an electric field the generated carriers will be lost[101]. Hertel[104] show experimentally by probing the fluorescence quenching, that generation of free electron – hole pairs in a single π-conjugate polymer is enhanced under the influence of an external applied electric field. This is of immense value in the plasmonic based solar cells where the strong plasmon electric field could enhance the excitonic dissociation process for generation of free electrons and holes. According to the Onsager concept, the energy of a singlet exciton in a single crystal molecule is insufficient to generate a pair of free charges where addition energy of 1eV is required[105]. That extra energy to free the electron-hole from the coulombic bounding can be provided via an
electric field or thermally activated diffusion process[105]. Thus for successful separation and charge collection the dissociation occurs in the junction of two materials where a strong electric field is present due to the different energies between LUMO and HOMO levels at donor and acceptor materials[106].

Another important difference between inorganic and organic based solar cells is the charge mobility and transportation in the materials. In organic solar cells the mobility is very low where excitons are dissociated near the interface of two materials hence the concentration of charges is expected to be high near the interface of two materials (Figure 3-9 a) [107]. On the other hand in inorganic material electron hole pairs are generated throughout the material thus the gradient of the carrier concentration across the device depth is smoother (Figure 3-9 b).

Figure 3-9 Different mechanisms of free electron-hole generation, their driving forces for transportation as well as the carrier’s concentration across the device a) for organic materials and b) for inorganic materials. Reproduced from [107].

The current density for a general excitonic solar cell device can be estimated using the same formulas for classical inorganic solar cells accounting the driving carrier
mechanisms for transportation in organic solar cells. Thus considering the driving
mechanism is the net effect of drift and diffusion processes the total current density
can be estimated from the following equation [107, 108]

\[ J_{\text{total}} = J_{\text{drift}} + J_{\text{diff.}} = \frac{eN\mu E}{A} + \frac{k_B T \mu \nabla p}{A} \quad \text{Equation 3-3} \]

where \( e \) is the elementary charge, \( N \) the concentration of charge carriers, \( \mu \) the
carrier mobility, \( E \) the applied electric field, \( k_B \) the Boltzmann’s constant, \( T \) the
temperature at device, \( A \) the active area of device and \( \nabla p \) the gradient in the
concentration of charge carriers. Equation 3-3 can be used to calculate either the
electrons current density \( J_e \) or holes current density \( J_h \) for both dark and light
conditions, by substituting the appropriate values for mobility, density of carriers
and gradient of concentration.

3.13.3 The equivalent circuit for solar cell

An ideal solar cell device can be modeled as a diode connected in parallel with a
current source representing the photocurrent \( J_{ph} \) (Figure 3-10 a). In dark conditions
the current density at diode \( J_{dark} \) can be calculated from Equation 3-4, representing
the leakage current [101]. For all equations below, the current per unit area, \( J \)
(density) is used.

\[ J_{dark} = J_{rev}(\exp^{\frac{eV}{k_B T}} - 1) \quad \text{Equation 3-4} \]

where \( J_{rev} \) is the reverse saturation current of diode, and \( V \) the potential difference
across the circuit. The output current \( J \) is the sum of all current in the equivalent
circuit, considering the leak \( J_{dark} \) is opposite to photocurrent \( J_{ph} \).
\[ J = J_{\text{dark}} - J_{\text{ph}} = J_{\text{rev}} e^{qV/k_B T} - 1 - J_{\text{ph}} \]  

Equation 3-5

At short circuit conditions in an ideal solar cell, the open circuit voltage is zero. Therefore from Equation 3-5 the short circuit current is equal to photocurrent \( J_{\text{sc}} = J_{\text{ph}} \). Furthermore at an ideal solar cell the open circuit voltage \( (V_{\text{oc}}) \) is given by Equation 3-6 [101, 103].

\[ V_{\text{oc}} = \frac{kT}{e} \ln \left( \frac{J_{\text{ph}}}{J_{\text{rev}}} + 1 \right) \]  

Equation 3-6

Figure 3-10 Equivalent circuits of solar cells a) ideal solar cell b) solar cell with integrated loss mechanisms (real solar cell).

In real solar cells losses exist, which can be represented as a resistor connected in parallel \( (R_{\text{sh}}) \) with the diode representing the recombination process in the solar cells and a resistor connected in series \( (R_s) \) with the rest of the circuit, representing losses from the ohmic resistance of front and back contacts (Figure 3-10 b). That circuit represents the I-V characteristic of a real solar cell. Thus the total current in real solar cells is the sum of photocurrent and losses given by
\[ J = J_{\text{dark}} + J_{sh} - J_{ph} \]  

Equation 3-7

\[ J = J_{rev} \left[ \exp \left( \frac{e(V - JR_s A)}{kT} \right) - 1 \right] + \left( \frac{V/A - JR_s}{R_{sh}} \right) - J_{ph} \]  

Equation 3-8

Form Equation 3-8 it is apparent that \( R_{sh} \) and \( R_s \) have to be infinite and zero respectively to achieve ideal performance.

Solar cells can deliver power when they operate in the fourth quadrant (0 to \( V_{oc} \)). The delivered power is the product of output current and voltage \( P = JV \), thus the maximum power is produced when the maximum current \( (J_{max}) \) and voltage \( (V_{max}) \) are delivered under the optimum load (Figure 3-11). The product of maximum current and voltage is called the maximum power point (MPP) \( P_{max} = J_{max} V_{max} \) denoting the optimum operating conditions.

The power conversion efficiency \( n_{eff} \) in any type of solar cell is defined as the ratio between the output electrical power over the power of incoming light given by Equation 3-9. Another figure of merit is the fill factor (FF) which represents the ideality of the solar cell under characterization. It is defined the ratio of the maximum power point to the theoretical maximum power of an ideal solar cell (Equation 3-10). Fill factor is directly influenced by loss mechanisms in solar cells such as the serial and shunt resistances.

\[ n_{eff} = \frac{P_{out(\text{electr.})}}{P_{in(\text{light})}} = \text{FF} \frac{V_{oc} J_{sc}}{P_{in(\text{light})}} \]  

Equation 3-9

\[ \text{FF} = \frac{V_{max} J_{max}}{V_{oc} J_{sc}} \]  

Equation 3-10
3.13.4 Surface plasmon enhanced solar cells

One factor which determines the amount of light absorbed in a photo-absorbing material is the film thickness. Beer’s law $A_b = \alpha L = -\log(I/I_0)$ implies that absorption $A_b$ is proportional to film thickness $L$ as the initial light intensity $I_0$ drops exponentially throughout the medium. However there is a trade off between the optimum thickness for complete absorption and maximum distance which carriers can travel before they recombine[40]. Conventional solar cells based on silicon have a thickness in the range of 200-300μm (wafer thickness) allowing an adequate quantity of impinging photons to be absorbed. A method to enhance further the absorption in conventional solar cells is to texture a few μm of the absorbing material surface. The textured surface scatters the incoming light at different angles, thus increasing its travelling path and the probability for absorption. For a material with refractive index, $n$, texturing can lead to enhancement up to $4n^2$ [40]. However this approach is
difficult to apply in thin films where the total active layer thickness is a few nm. Incorporation of metal nanoparticles with size smaller than the wavelength of the AM1.5 spectrum to excite localized surface plasmons and utilizes their effect to handle efficiently the incoming light is an alternative well promising solution [24, 42, 109, 110].

Stuart and Hall [25] in their pioneering work in 1996 on photo-detectors which were fabricated in a silicon on insulator (SOI) structure showed that the performance of devices improved by decorating them with metal nanoparticles on the front surface which enables better coupling of light into the silicon. Furthermore, Hohenau [111] in 2005 show experimentally that illuminating a silver particle with light, excites strong electric fields and radiative light through leakage radiation processes near its surface (Figure 3-12).

![Figure 3-12 Surface plasmon E field excited at the vicinity of an Ag particle with a) p-polarized and b) s-polarized light, reproduced from [111].](image)

In the following years a large amount of research was carried out to determine how strong electric field and light scattering could influence the photovoltaic processes and enhance the device efficiency. Through those research findings, the
performance enhancement in solar cells from surface plasmon excitations can be divided in three different categories. The different enhancements categories are distinguished depending on the place where the particles are located into the structure and which is their dominant extinction component. The scattering or absorption of light near the resonance wavelength of the particles depends strongly on the size of the particles. Metallic NPs smaller than 10nm tend to absorb more, hence extinction is dominated by absorption in and very close to the metal particles, while for bigger particles, extinction is dominated by scattering[42].

In the first category metal nanoparticles are used as a matching optical impedance medium to allow energy momentum conservation[42]. Typically known as antireflection coating it is placed only at the front side of solar cells[112]. It has been demonstrated that a mixture of common antireflection material such as 50nm thick Si$_3$N$_4$ with metal Ag based nanoparticles arrays with their size are in the range of 125nm and their separation pitch at 450nm is the optimum structure for this category [113].

![Image](image.png)

**Figure 3-13** Antireflection coating based on a mixture of common antireflection materials and metal nanoparticles, reproduced from [113].
The generic nature of this concept allow the method to be integrated both in organic and inorganic solar cells.

The second category is similar to that previously mentioned but with major difference that the particles are integrated at different layers in the photovoltaic device structure promoting the forward scattering[40] and effective light travelling path[114, 115].

![Diagram](image)

**Figure 3-14** Uncoated particles into the bulk hetero-junction (BHJ) active layer cause scattering of light resulting in increased absorption path. Reproduced from [114].

The high contrast between the refractive index of metal nanoparticles and the surrounding medium works like very fine waveguides coupling efficiently the light (forward scattering) in the near vicinity of particle which can be the absorbing layer[40]. Silver particles deposited with electro-deposition in a buffer layer between ITO layer and the polymer based active layer are demonstrated to enhance the overall device efficiency by 4% [110]. Similarly Au particles blended in PEDOT:PSS and spin coated improved the efficiency [116, 117]. Studies with integrated uncoated Au or Ag particles into polymer based active layers have shown improvement in power conversion efficiency [114, 115] however, there is a contradiction with other
studies which report efficiency suppression due to recombination process which takes place on the surface of the uncoated metal particles [118].

The third category is involving enhancement induced from the strong electric field which is exhibited by localized surface plasmon resonance at metal particles. As was mentioned in the previous section, the strong E field can enhance the exciton dissociation and charge transportation[105]. In this category small particles <10nm are required where the absorption component is dominating inducing strong electric fields.

![Diagram showing exciton dissociation and recombination](image)

**Figure 3-15** The effect of SPR on excitons, resulting in an enhanced rate of excitons dissociation process.

Reproduced from [117]

Kulkarni and co workers demonstrated experimentally that silver nanoparticles with strong SPR can be used into poly(3-hexylthiophene)/phenyl-C60-butyric acid methyl (P3HT/PCBM) to enhance successfully the charge carriers generation[119]. Due to the nature of the process it is predominantly associated with polymer material solar cells although enhancement for a-Si:H is also reported[120].
3.14 Device application two: Sensors based on metal nanoparticles

There is a surge of interest in sensors technologies due to constant increasing demand in healthcare, automotive, metrology and several other sectors, for sensors which comprise higher reliability, sensitivity, smaller size and lower cost. Concomitantly sensor technologies are a hot topic among the scientific and engineering communities with a large margin for improvements which demands intense research[8]. New concepts and fabrication methods based on nanotechnology for bottom-up fabrication are expected to improve the performance of established systems, meanwhile new innovative systems with improved sensitivity, selectivity and ability for multiple elements analysis are developed.

Independently of the technology which is used, the quality of a sensor and its performance are determined by key factors of sensitivity, selectivity and response time.

The sensitivity $S_n$ of sensor, known as its transfer function, describes the output signal $y$ as a function of the input signal $x$, determining the ability of the sensor to detect a specific concentration of the element to be detected[121].

$$S_n = \frac{dy}{dx}$$  \hspace{1cm} \text{Equation 3-11}

The sensitivity is directly related with the sensitivity factor where it is defined as the ratio of the output at low concentrations over the output at high concentrations [122] and is normally used for calibration purposes.
Selectivity $S_i$ is the ability of a sensor to detect distinguishably and accurate one measuring element within a mixture of different measuring elements. Selectivity can defined by the cross sensitivity of all other elements which occur with a concentration $x'$ over the sensitivity of sensor for the specified measuring element within the mixture[8]. Thus,

$$S_i(\%) = 100 \times \frac{dy/dx'}{dy/dx}$$  \hspace{1cm} \text{Equation 3-12}

The response of the sensor is defined as the change of the output value with respect to initial value over time, after applying different concentrations of the measuring element in a step function[8]. Hence response is given by[123]

$$S_r(\%) = 100 \times \frac{y_0 - y(t)}{y_0}$$  \hspace{1cm} \text{Equation 3-13}

where $y_0$ is the initial measured value and $y(t)$ is the measured value after time (t) when a new concentration of the element to be detected is applied.

Metal nanoparticles are excellent candidates for sensing technologies due to their unique catalytic, electronic and optical characteristic properties.

Based on these properties MNFs sensing elements can be distinguished in two major categories. In the first category sensors are based on the electrical properties while the second category is based on the optical properties of metal nanoparticles.

### 3.14.1 Electrically based MNF sensors

A major class of commercial sensing elements are typically using nanoparticles to tailor their output electrical characteristic. An example is the resistive gas-sensors.
Resistive sensing elements use metal or metal oxide particles where a change of their electrical resistance occurs when a gas is applied. In percolated films with metal oxide particles, the interaction of their surface with the target analyte changes the electrical resistance of the conduction path. Typically materials such as SnO$_2$, ZnO, WO and In$_2$O are used [8, 124]. A shift in their state of equilibrium on the surface oxygen occurs, induced by the presence of the target gas. Depending on the gas nature reducing or oxidizing O$_2$ is chemisorbed on the surface predominantly as ions. These acts as electron acceptors or donors due to their relative energetic position with respect to Fermi level $E_F$ leading to an electron depleted or enriched surface region called space charge region $\Lambda_{air}$ [8].

The change of electron density at the surface bends the outer bands forming a potential barrier $eV_{surf}$ in the order of 0.5 to 1eV[8]. Between particles the $eV_{surf}$ works as schottky barrier affecting the conductance $\sigma$ of the film.

$$
\sigma \approx \exp\left(\frac{-eV_{surf}}{k_B T}\right)
$$

Equation 3-14

The larger the surface to bulk ratio the more gas atoms interact on the surface, thus one should expect that size of particles would affect the sensitivity of sensor.
Figure 3-16 Change of potential barrier’s height when gas molecules interact with the absorbed oxygen on the surface of metal oxide particles, reproduced from [124]

There is a vast number of experimental and theoretical works showing that the use of appropriate particle size for each gas yields, increased the sensitivity as well as faster response time[125]. Furthermore it was been demonstrated that besides particle’s size, porosity and thickness of the film contribute significant into the response time.

Sensing elements based on metal nanoparticles are similarly popular in commercial applications. In these structures metal nanoparticles are coated with organic ligands to target specific gases or vapours while the metal particles are providing an adequate conductive path[8]. Moreover structures with plain nanoparticles have been demonstrated to sense gases which are known to be reactive with the particle’s metal[126].
In these hybrid systems the conductivity can be modelled according to an activated charge transport mechanism which is amenable by activation energy $E_a$. The mechanism can be either hopping charges between neighbouring particles[45, 49] or electron tunnelling[53] elaborated in chapter 2. The dominant charge transport mechanism, which is responsible for conductivity in a particular structure is determined by the size of particles, the interparticle separation distance, and the surrounding medium.

### 3.14.2 Charge hopping sensing elements

Charge hopping in a structure can be conceived as a classical redox process in molecular matrixes constituted of outer and inner clusters[127]. The chemical reaction of gases with the reactive part (molecules or metals) leads to oxidation or reduction in an “outer sphere” which is associated with charge transfer through the bridging ligand “inner sphere”. Zamborini [45] demonstrated ethanol vapour and N$_2$ sensing with Au particles in a mixture of alkenethiolate and carboxylate polymer. Furthermore conductivity dependence with the polymer chain-length has been observed in this work. A striking approach of high sensitivity metal nanoparticle based gas sensors has been demonstrated by Star[128], Yun[129] and Sun[130]. In these works metal particles are used as reactive elements on top of carbon nanotubes (CNTs) to target a wide range of specific gases and change the conductivity of CNTs in a similar manner as the one described for ligand encapsulated particles.
3.14.3 Electron tunnelling sensing elements

For structures where electron tunnelling is dominating, the conductivity follows Equation 2-24. The term $e^{-S\phi}$ denotes the electron tunnelling between particles and is exponentially depending on the separation distance between particles[8]. Hence for functionalised particles in polymer matrices the chain length of the attached molecule determines mainly the initial conductivity. The second exponential term $e^{-E_a/kT}$ denotes the activation energy in the system[8].

Varying the number of embedded Au nanoparticles in polyelectrolyte multilayer (PEM) film with thickness up to 6.5nm it has been observed that it changes the charge transfer mechanism from electron tunnelling to electron hopping[7]. Gold particles functionalized with thiols shows excellent response and recovery to NO₂ gas[53]. Trithiol capped Au particles are reported to be more stable in ambient conditions for longer time and they show good sensitivity to toluene, ethanol, methanol and acetone vapours[52]. Similarly with gold–propyleneimine composite films propanol, toluene and water vapours are detected[131]. Palladium nanoparticle arrays within interdigitated electrodes have been demonstrated to give good hydrogen sensing elements[14, 126]. Pd nanoparticles are very reactive with H₂[132] forming PdHₓ[133]. Adsorption of H₂ on the Pd surface dissociates it to atomic H where on diffusion into the bulk Pd forms PdHₓ increasing particle’s volume[134]. That increase in volume changes the spacing between particles thus the current flow change according to Equation 2-22 and Equation 2-24. Similar structures have been rigorously studied by a number of different groups.
demonstrating coulomb blockage and Coulomb staircase at room temperatures, characteristic phenomenon of electron tunnelling [4, 6, 135].

3.14.4 Optical based metal nanoparticle sensors

Noble metal nanoparticles exhibit unique optical properties associated with the local surface plasmon response (LSPR) as described previously. That resonance causes strong absorption or scattering of light and an enhanced electric field in the near vicinity of the particle. The LSPR is directly dependent on the nanoparticles’ material, their physical dimensions as well as the surrounding medium. Over the years two steams of metal nanoparticle based optical sensors have been developed to detect primary gases and molecular assemblies without using labels: Those which are based on the shift of LSPR peak by changing the dielectric of the surrounding medium[136] and those which are based on enhancing the Raman signature of the under detection specimen due to the strong electric field.

3.14.5 Local surface plasmon resonance optical sensors

The metal nanoparticles used in this type of optical sensors exhibit a known optical extinction peak at the plasmon resonance frequency. The intensity and frequency of this peak is dependent on the surrounding medium. Any variation in the refractive index of that medium caused be introducing a gas or molecules diluted in a solution leads to a change in the extinction’s peak intensity and position. The working principle of these optical sensors relies on the particles’ LSPR variation which is
detectable. Normally a prism, coated with noble metal nanoparticles at one side is used to measure the reflection of the incident light (Figure 3-17) although other methods such as optical fibers[137] are reported.

Figure 3-17 Graphical illustration of a metal nanoparticle coated prism, used in optical sensors for monitoring the changes of LSPR.

For frequencies in the visible regime $\gamma<\omega_p$ [136], hence Equation 2-2 can be simplified to

$$\varepsilon_m = 1 - \frac{\omega_p^2}{\omega^2}$$

Equation 3-15

The surface Plasmon resonance peak appears in the frequency range where the $\varepsilon_m=-2\varepsilon_d$ condition is fulfilled. Substituting the dielectric constant of metal $\varepsilon_m$ in Equation 3-15 with the dielectric constant of surrounding medium $\varepsilon_d$, the shift in LSPR frequency for variation of the refractive index $n$ can be obtained from Equation 3-16, since $\varepsilon_d=n^2$[136].
\[ \omega_{spr} = \frac{\omega_p}{\sqrt{2\varepsilon_d + 1}} \]  

Equation 3-16

The same technique can be applied similarly for bulk metal films, where using a prism to couple the light the shift of bulk SPR frequency imposed by different environments can be detected. However, it is reported that use of particles and monitoring of LSPR is better compared to bulk metal films and bulk SPR due to its simplicity and lower cost[136, 138].

Functionalized alkenethiol molecules and biotin-avidin biological solutions with concentrations down to 1mM are reported to be detectable in real time with good sensitivity and response times using SiO₂ substrates coated with gold nanoparticles [137]. Pulsed laser deposited alloy MNFs of Au-WO₃ using two separate source targets to fabricate composite MNFs on glass substrates, demonstrated adequate capability to sense nitrogen monoxide (NO) gas[139]. Concentrations down to 1000ppm could be detected by recoding the SPR response (reflectance intensity), where the tungsten oxide (WO₃) was used to enhance the sensitivity of Au particles to NO since it known that noble metals are not reactive to many gases[139].

3.14.6 Surface enhanced Raman spectroscopy optical sensors

Nobel metal nanoparticles exhibit a strong localized electric field upon light illumination which can be utilized to enhance certain process such as fluorescence and Raman scattering. The Raman signal is generated from the inelastic scattering of photons upon their interaction with matter, and it was discovered by Venkata
Raman in 1928. Raman spectroscopy itself is very promising technique for label free sensing due to the unique signature of each specimen. However its low probability of occurrence, known as Raman scattering cross section $10^{-31} \text{ cm}^2/\text{molecule}$, produces a weak signal. Hence an amplification method is necessary, particularly in specimens with low concentrations, to circumvent the low levels of signal. Metal nanoparticles with sharp SPR exploit highly amplification of electric field and consequently of Raman signal. That process is known as surface enhanced Raman scattering (SERS) and it is reported that an enhancement of the scattering cross section $\sigma_{RS}$ by a factor $10^{14}$ can be observed [26, 140]. Elucidation of that process is presented in the following sections.

In the Raman effect the inelastic vibrational scattering of photons is imposed from the molecular vibrations. Generally Raman involves energy gain on loss of the associated photon, known as antiStokes or Stokes, respectively. The incoming photon with energy $h\omega_L$ is scattered inelastically from a vibrating molecule. Due to this vibration interaction, the photon’s energy is shifted by $h\omega_M$ affecting its original frequency (Figure 3-18). The frequency shift can be in both directions depending on molecular state. For a molecule that is in its vibrational ground state, the photon loses energy (decrease frequency to $\omega_S$) by exciting vibrations in molecular known as Stokes scattering, while if the molecule is in a vibrational excited state the photon appears to gain energy (increase frequency to $\omega_{as}$) known as anti-Stokes scattering[1, 27].
Figure 3-18 Graphical representation of Raman signal generation where the frequency of the associate photon it is shifted depending on loss or gain of energy where Stokes or anti-Stokes scattering is generated.

Therefore the frequency of those two Raman band can be estimated according to following equations [1].

\[ \omega_S = \omega_L - \omega_M \]  \hspace{1cm} \text{Equation 3-17}  \\
\[ \omega_{as} = \omega_L + \omega_M \] \hspace{1cm} \text{Equation 3-18}

The most important characteristic of Raman effect is the absence of absorption or emission of photons, any involvement of energy transition is purely from the scattering process and it can described as spontaneous scattering event[1]. A direct consequence is the so called resonance Raman signal (RRS) where the frequency of pump laser is in resonance with the energy transitions in a molecule (Figure 3-19). In this case the Raman signal (RS) is relatively stronger, however, compared to fluorescence (a stimulated process) it is much weaker. Indicatively, the cross section for RS is $10^{-31}$ for RRS $10^{-29}$ cm²/molecule while for fluorescence which is dependent on the absorption and fluorescence, quantum yield can reach $10^{-16}$ cm²/molecule[27].
Figure 3.19 Illustration of the different processes which are involving photon interaction with molecules.

The Raman signal is based on the vibration levels of molecules which are determined by their size, their internal structure of atoms, their bond strength and their spatial distribution. Therefore Raman can probe the signature of each different type of molecule precisely [27]. Thus Raman spectroscopy is ideal for label free sensing applications where fast and reliable diagnosis of data is required.

For the explanation of RS amplification with SERS, the light is considered as an impinging electromagnetic wave which induces a dipole moment in the molecule. Thus due to the molecule’s vibrational modes that dipole moment is modulated. According to classical modulation theory the modulated carrier signal (excitation source light) appears to have two sidebands due to the modulation envelope which in this case can be considered as the Stoke and anti-Stokes frequencies[27]. Hence the power of “side lobes” is linearly proportional to the intensity of the excitation laser beam $I(\omega)$. The total power of one side band assuming the Stokes band $P_S$ can be calculated from
\[ P_S(\omega_S) = N_m \sigma_{RS} I(\omega_L) \] \hspace{1cm} \text{Equation 3-19}

where \( N_m \) is the number of molecules within the laser spot area.

In SERS, an enhancement of the above process occurs, so that \( P_{SERS} > P_S \). For the amplification metal nanoparticles or a thin metal film with sharp perturbations which can exhibit SPR, at pump’s laser wavelength are used in the specimen with the questioning molecules.

Theoretical studies suggest that part of the enhancement is attributed to the chemical interaction of molecules with the metal leading to an increased scattering cross section \( \sigma_{SERS} \) in the order of 100[1, 141]. However it is generally accepted that a more dominant role in the enhancement process holds the strong field which develops around nanoparticles due to LSPR. This field is reported to enhance both the incoming (pump laser beam) and emitting (Raman signal) fields with factors \( A(\omega_L) \) and \( A(\omega_S) \). Thus the amplified Raman signal for Stokes band can be expressed as[27]

\[ P_S(\omega_S) = N_{SERS} \sigma_{SERS} A(\omega_L)^2 A(\omega_S)^2 I(\omega_L) \] \hspace{1cm} \text{Equation 3-20}

where \( N_{SERS} \) is the number of molecules under the influence of electric field which appear in the particles’ vicinity.

Having considered the excitation light as an electromagnetic field, the local intensity of electric field \( E_{loc} \) which is experienced by a molecule positioned at distance \( d \) far from a metal particle with radius \( r \) will be the superposition of electric fields from light \( E_0 \) and metal particle \( E_{spr} \). Concomitantly the amplification factor \( A(\omega) \) will be the ratio of the local superposition electric field over the initial field from pump laser expressed in the following equation[27].
\[ A(\omega) = \frac{E_{loc}}{E_0} \sim \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2 \varepsilon_d} \left( \frac{r}{r + d} \right)^3 \]

Equation 3-21

Because the maximum polarization in a metal occurs at the LSPR peak one should expect that the maximum amplification in SERS will appear when the wavelength of the excitation light is both at the same frequency as the LSPR peak and is in resonance with the molecule’s vibrational modes\[142]\) in order for RRS to take place. Furthermore since the dielectric constant of the surrounding medium is involved in gain, different amplification factors should be expected in the same system for materials with different dielectric constant or refractive index, a principle which has been validated experimentally\[143]\).

Substituting Equation 3-21 in the amplification factors at Equation 3-20 the total enhancement from laser and Stokes field can be expressed as\[27]\)

\[ A_{tot}(\omega_S) = A(\omega_L)^2 A(\omega_S)^2 \sim \left( \frac{\varepsilon_m(\omega_L) - \varepsilon_d}{\varepsilon_m(\omega_L) + 2 \varepsilon_d} \right)^2 \left( \frac{\varepsilon_m(\omega_S) - \varepsilon_d}{\varepsilon_m(\omega_S) + 2 \varepsilon_d} \right)^2 \left( \frac{r}{r + d} \right)^{12} \]

Equation 3-22

This equation denotes that for SERS enhancement it is not necessary for the molecule to be attached to the particle, however, the amplification decays very fast with increasing distance\[27, 142]\).

In cases where multiple particles exist on the specimen under examination, a molecule between two neighbouring particles will experience the influence of electric fields from both particles. The total electric field at the middle point between two particles will be a superposition of the electric field from light \(E_0\) and the LSPR induced electric fields from both metal particles \(E_{spr1}\) and \(E_{spr2}\) respectively. Thus the field’s strength at that point will be very strong, known as “hot spot”\[144]\). Typically very high electric fields are found for separations below 5nm\[141]\). It is reported that
the sharper the metallic features at one edge and the closer spaced the stronger the enhancement[27]. Metal gold nanostars with very sharp edges and a monolayer of 4-mercaptobenzoic were used in SERS experiments estimating an enhancement factor of $10^7$ for individual nanostars[145].

An interesting approach is proposed by Oates [146] where silver particles with different thickness gradient are deposited on plain glass coated with Rhodamine 6G (R6G). They are reporting different enhancement factors proportional to the gradient. Altering the thickness gradient implicates the SPR peak position. Hence different coupling efficiencies of the SPR induced electric field with R6G molecules infer different Raman amplifications.

Amorphous carbon on Si and glass to form rough surfaces deposited with pulsed laser deposition and then coated with silver at different thickness to create metal islands is reported to give SERS and fluorescence enhancements from R6G and protein bovine serum albumin labelled with fluorescent isothiocyanate (BSA-FITC)[147]. Furthermore the same authors have shown that silver particles formed from UV photo-reduction of AgNO₃ printed directly on low cost borosilicate microscope cover glass could give 100 fold enhancements in the photoluminescence and SERS signal from R6G solution with concentration 20µM[56].

A graphene slab mounted on SOI substrates and coated with a square array of Au particles is reported to significantly enhance both G and 2D bands when excited with a 633nm laser. They found that Raman signal scales up exponentially with the particle cross section and decreases with the separation between particles and graphene[148].
In spite of studies with metal nanoparticles, angle resolved SERS enhancement has been observed in bulk metal films with uniform arrays of holes fabricated using interference lithography. For the Raman study molecules of 6-mercaptopurine were used, reporting increase of Raman signal by increasing the hole diameters up to 400nm[149].
4 Experimental techniques

In the following sections the process and equipments which were used to fabricate devices and thereafter characterize them are presented.

4.1 Device fabrication with rapid laser annealing

For all laser annealing processing which was performed during this project, to fabricate metal nanoparticles, a KrF excimer laser from Lambda Physics (LPX210i) was employed. Excimer lasers belong in the group of pulsed lasers. For lasing they excite diatomic molecules with short electronic transition life time to emit coherent laser light. The short life time of the excited transitions is attributed to the repulsive force between the two atoms of molecule in its ground state[150].

Excimer laser typically consist of a rare gas Ar, Kr, or Xe mixed with a halogen gas such as F, Cl, Br or I. The excitation is induced through electrical discharge between the metal electrodes where up to 5% of the applied energy can be converted to light. Depending on the gas mixture excimer lasers can emit at different wavelengths, typically XeF at 353nm, XeCl at 308nm, KrF at 248nm and ArF at 193nm. The pulse duration during light emission, ranges between 10 to 50 nanoseconds with delivered energy of 0.1-1J [150]. Excimer lasers can operate at repetition rates up to kilohertz.

Due to the corrosive nature of halogen gases the entire laser cavity is normally built within a stainless steel cylinder coated with polyvinyl and Teflon. A gas recirculation system is connected to the cavity for refilling and purifying the gain material. The electric energy is mediated into the gain material through a capacitor discharge
transverse to the electrodes. Reflection mirrors of 100% and 80% are typically used at the back and front ends of the cylinder respectively to provide optical feedback in the gain material for stimulated emission. Figure 4-1 illustrates a typical Excimer laser structure.

![Figure 4-1 Typical structure of Excimer laser with two mirrors for optical feedback and a gas processing system.](image)

### 4.1.1 Optical configurations for laser nanostructuring

Two different optical configurations were used for the laser system in this project. The first configuration allows relatively large laser spots to raster large areas quickly while the second configuration results in narrow laser spots down to 5-20μm for writing very fine patterns.

The first optics configuration is presented in Figure 4-2. A laser beam homogenizer is utilized to distribute evenly the power density across the spot’s width in order to minimize excess thermal effects during the annealing in some areas. In addition, the homogenizer attributes a Gaussian like power distribution across the beam spot long axis. Thereafter the laser beam is guided with appropriate mirrors though an
aperture to form a sharp rectangular spot which is focused on the substrate’s surface utilizing a focusing lens. The laser fluences which are quoted in this manuscript are for a single pulse. The quoted fluences are expected to have at least 10% error due to calibration uncertainty of 3% at thermopile detector from Coherent Ltd (1/4-20 M6) and an error of 6-9% from the pulse-to-pulse variation produced by excimer laser. The pulse duration is 25ns according to manufacturer’s specification. For all annealing work which was performed using the first optical setup (large size spot) a laser beam spot of 4x3mm² was used. The overlap between two spots was kept at 10% of the beam length. The repetition rate which was used for each experiment is quoted in each individual Chapter.

During laser annealing the samples are processed in a direction parallel to the Gaussian distribution axis. Due to Gaussian like power distribution across the spot, the laser fluence, and consequently the thermal effect, are different for each point
across this axis. For a simple Gaussian shaped beam the transverse distribution of light intensity $I_L$ at any point it is given by [150]

$$I_L = I_{L_{(\text{max})}} e^{-2x^2/w^2} \quad \text{(Equation 4-1)}$$

Where $I_{L_{(\text{max})}}$ is the maximum intensity, $2x$ the beam’s dimension along the Gaussian axis and $w$ the “beam waist” inside of which 86.5% of the total energy is included as presented in Figure 4-3.

![Figure 4-3 Energy distribution for an ideal Gaussian shaped laser beam.](image)

The total delivered power density from a Gaussian beam it can be calculated using the sum of all light intensities from the centre of outer radius of beam across the beam multiplied by its width $z$.

$$\text{Fluence} = \left( 2 \sum_x I_L(x) \right) z \quad \text{(Equation 4-2)}$$

However the beam profile for the Excimer laser used in this project is asymmetric [151] with its intensity to increase at its maximum sharply. For simplicity in the following chapters the energy recordings measured with the thermopile detector are assumed to be of uniform profile affecting slightly the fluence value.
Assuming that only the area of beam which the 86.5% of energy is concentrated induces the desired thermal effect and this area is equal to the 86.5% of total spot area a more realistic estimation of the actual fluence would be given by dividing the measured energy with the a reduced area given by

\[ \text{Fluence} = \frac{\text{Measured energy}}{0.865 \times 2x \times z} \]

Equation 4-3

For narrow paths the second optics configuration presented at Figure 4-4 were used. In this configuration a reflective objective lens from Edmund optics (NT58417) as displayed in the inset of Figure 4-4, was used to achieve high resolution beam focus. The high resolution beam was used to write narrow paths on the sample under processing. In this type of beam concentrating objects, the light enters in a cavity with two confocal mirrors. These mirrors waveguide the light to focus within a very fine spot close to diffraction limits. Furthermore the use of mirrors to focus the light eliminates problems such as spherical-chromatic aberration and material absorption allowing more efficient management of the delivered energy. This configuration was used to write the final successful interdigitated patterns to form the sensing elements described later at chapter 7. For this work a circular beam spot was used with a diameter of 20μm and no overlaps between two sequential spots. More details about the necessary laser fluence and other parameters are included in Chapter 7.
4.1.2 Solar cells device fabrication

In this section an overview of the process step for solar cell device fabrication is undertaken. A more detailed analysis of the parameters which were used for each step is presented later in chapter 6. In this section more emphasis is given to the critical processing parameters which are required during the laser annealing to fabricate metal nanoparticles for successfully working photovoltaic devices.

For plasmonic solar cell fabrication commercial rectangular glass substrates with dimensions 15mm X 15mm were used. The glass substrates were acquired pre coated with Indium Tin Oxide (ITO) forming a strip with dimensions 15mm X 9mm as Figure 4-5 illustrates. After cleaning the substrates a thin film of 35nm Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate) (PEDOT:PSS) was coated with a spin coater (Laurell Technologies WS400B-6NPP-LITE) followed by a thin metal film deposition using thermal evaporation. The structure was laser annealed to form metal nanoparticles and a second layer of PEDOT:PSS was spin coated to cover the
particles. Thereafter a solution with a mixture of poly(3-hexylthiophene) (P3HT) : phenyl-c61-butyric acid methyl ester (PCBM) was spin coated to form the active layer followed by two layers of bathocuproine (BCP) and Al thermally evaporated through a shadow mask to form the back contact.

Figure 4-5 All process steps for laser induced direct writing of plasmonic substrates for polymer solar cells fabrication.

The critical factor for successful operating solar cells is the direction that laser annealing is performed with respect to ITO layer. Although a beam homogenizer is used, in reality the power distribution at some point in the beam is slightly higher. The power distribution along the long axis of the beam is Gaussian. Along the short axis the power distribution is relatively constant. However, at some point the power is higher caused by small damage at the optics, making the power distribution along the short axis uneven. For more information the reader should also refer to [152].

During the scanning process, these regions of this higher intensity induce excess damage in the ITO layer forming strips with different conductivity (Figure 4-6). The direction of those strips with respect to electron flow can influence the electrons’ extraction efficiency. This can lead to performance degradation depending on the
position where the electrodes for performing the I-V measurements are contacted. Those probes are attached at the ends of ITO strip along the long axis (15mm). The laser rastering for high performance solar cells was performed along the long axis to allow formation of current flow paths with uniform low resistance which allow efficient charge collection (Figure 4-6 a). Vice versa, laser annealing along the short axis resulted in a network of resistors connected in series increases the series resistance of device $Rs$ reducing its overall performance (Figure 4-6 b).

![Diagram showing laser annealing along long and short axis](image)

**Figure 4-6 Resistance of ITO substrates depending on the laser annealing direction**

The laser annealing direction can significantly affect the resistance of the ITO film. Annealing performed along the long axis of ITO substrate allows good charge extraction while annealing performed along the short axis of ITO forms a network of series resistances which introduce excess losses at charge extraction-collection.

Another important parameter is the resistance at the contact points on ITO film where the electrical probes are attached. To keep at minimum the contact resistance, a mask was used to cover the areas of ITO where the electrodes are attached to prevent any damage from the laser annealing process. Laser annealing
these areas increases the contact resistance leading to performance degradation. The areas where the mask was used on ITO are highlighted with red at Figure 4-6.

### 4.1.3 Thermal evaporated metal deposition

The metal deposition of thin films was performed with a multi crucible vacuum thermal evaporator (Edward 306). The deposition of metal films was performed at low and relatively constants rates (0.1 -0.2 Å/s) to obtain films with uniform thickness. During evaporation the vacuum was maintained at 1.0x10⁻⁶ Torr to allow a free travelling path for metal vapours from collisions with background gases. The metal for deposition was placed into heating filaments made of tungsten. The filaments were heated electrically to allow evaporation.

The deposition rates were monitored with a thickness monitored (Intellemetrics IL 50) connected to the evaporator. The thickness was monitor with an oscillating quartz crystal. The mass of the deposited material on the surface of quartz causes a change in the oscillation frequency of crystal. Lu [153] show that the thickness of the deposited material can be derived from the following equation.

\[
\rho_f t_f = \left( \frac{\rho_q v_q}{2\pi Z f_c} \right) \tan^{-1} \left\{ \tan \left( \frac{\pi (f_q - f_c)}{f_q} \right) \right\} \tag{Equation 4-4}
\]

Where \(\rho_f\) is the density of measured film, \(t_f\) the thickness of the film measured \(\rho_q\) the density of quartz, \(v_q\) the velocity of acoustic wave through quartz, \(Z\) the acoustic impedance factor, \(f_q\) the oscillation frequency of uncoated quartz, \(f_c\) the oscillation frequency of coated quartz.
4.2 Material characterization

4.2.1 Optical absorption spectroscopy

For the metal nanoparticles films optical characterization a UV – VIS – IR spectrophotometer (Varian Cary 5000) was used to record the absorption as a function of wavelength. Generally the light intensity attenuates when light traverses a material due to optical absorption in material. That attenuation is described by Beer-Lambert’s law (Equation 4-5), furthermore at MNFs an extra nonlinear absorption occurs owning to the surface plasmon effect at metal nanoparticles as described in previous chapters.

\[ I(x) = I_0 e^{-\alpha x} \] \hspace{1cm} \text{Equation 4-5}

\[ A_b = \log \left( \frac{I_0}{I} \right) \] \hspace{1cm} \text{Equation 4-6}

where \( I_0, I \) are the intensity of impinging and attenuated light respectively, \( \alpha \) is the absorption coefficient and \( x \) the film thickness. “\( A_b \)” is the calculated absorbance defined by Equation 4-6. The Cary 5000 spectrometer has two light sources a mercury and a tungsten lamp for UV and VIS light sources respectively. The light is guided through a monochromator for wavelength selection. The transmitted light traverses both the sample and the reference is modulated with a chopper to minimize errors from the neighbouring light sources. The collection of two optical signals occurs onto a light detector which it determines the absorbance.
4.2.2 Fluorescence spectroscopy

The characterization of fluorescence from solar cell structures was performed with a Cary Eclipse spectrometer from Varian. Fluorescence measures the luminescence exhibited by molecules when they are excited by UV-VIS-IR radiation. Part of the absorbed energy is transformed into luminescent light when electrons from an excited state drop back to the ground state releasing the extra energy by light emission. Thus by stimulating a molecule with light and measuring the amplitude of fluorescence presents a figure of merit about the electron quenching which occurs. Electron quenching in photovoltaic structures is related to the exciton dissociation process analyzed more within chapter 6.

The light in the Cary Eclipse is provided by a xenon flash lamp. A monochromator is used to determine the correct light wavelength which excites molecules under detection. While the molecules are excited a scan across a range of wavelengths is performed to collect the luminescent signal with an optical detector which operates in avalanche configuration for better detection of weak signals.

4.2.3 Raman spectroscopy

Raman spectroscopy has been employed to measure the enhancement of R6G Raman signal induced by SERS active substrates and to compare the amount of P3HT crystallization [154] after thermal annealing. A Micro-Raman 2000 from Renishaw was used to acquire the Raman signatures. The system can operate using two excitation laser wavelengths (782nm or 514nm). The laser beam is focused on the samples surface using a focal lens to excite the molecules. The combination of back
scattered Raman signal where its wavelength is slightly shifted due to the vibrations at molecules (inelastic scattering) described previously in Chapter 3, in addition with the photons from elastic scattering known as Rayleigh scattering are back collected from the same focal lens. Thereafter the signal passes through a narrow band stop (Notch) filter to remove the initial laser excitation wavelength from the Raman signal. The filtered signal is displayed on gratings where the spectral intensity of light is recorded with a CCD camera. The acquired image is converted to frequency domain using Fast Fourier Transformation (FFT) to extract the Raman signature. Typically the laser power is held below 5mW to minimize damage to the sample. The active depth of investigation is determined by the absorption coefficient of the material under study for the laser wavelength which is used. Normally that depth is in the range of 1μm.

4.2.4 Scanning electron microscopy

High resolution images of the laser annealed surfaces were acquired with a scanning electron microscope (SEM) from FEI (Quanta 200 F) to analyze their morphology and to characterize the particles’ dimensions and composition. An electron beam with energy ranging from 0.2KeV to 40KeV is emitted at low vacuum from an electron gun, normally made of tungsten electrode. The electron beam is guided and focused with a magnetic condenser lenses which it can go down to a spot size approximately 5nm in diameter. The electron beam is deflected to scan the surface using electrical deflection plates. The emitted electrons collide on the sample surface generating secondary back scattered electrons by inelastic scattering and X-rays. For capturing an image the back scattered electron are accelerated towards a scintillating surface
which emits light when electrons collide. The light is multiplied and captured by a photo-detector to form the image. The produced X-rays are used for quantitative X-ray analysis known as Energy Dispersive X-ray spectroscopy (EDX) where the elemental composition of the material under detection can be determined. With SEM, images of great depth analysis and high magnification can be acquired.

4.2.5 Atomic force microscopy

An atomic force microscope (AFM) from Digital Instruments Dimension (3100 AFM) was used to scan the surface of laser treated specimens and determine their morphology and surface roughness. For all AFM images in this project the microscope was used in tapping mode to acquire them. AFM is a scanning probe technique which can acquire high resolution images at the nanometer scale. A cantilever with a sharp vibrating tip taps the surface while it is moving across the sample in raster mode. For a tip oscillating at a constant frequency the deflection of the tip change as it approaches a surface due to interaction by Van der Waals, electrostatic or magnetic forces. To obtain an image the deflection of the cantilever is monitored optically with a laser beam pointed at the tip. The position of the reflected laser beam is recoded on a photodiode array where the signal is processed for the image reconstruction.
4.3 Devices characterization

4.3.1 Power conversion efficiency for solar cells

For the electrical characterization of the fabricated photovoltaic devices a Keithley 2400 source-meter was used, combined with a class B sun simulator from Oriel 81160 for light exposure according to the CEI/IEC904-1 (1987) standard. The Oriel simulator is fitted with a xenon lamp and an Air Mass 1.5 Global (AM1.5G) filter to provide light with \( \leq 5\% \) of non uniformity. The delivered power of sun simulator can be calibrated by adjusting the electrical power and the position of the lamp. The calibration of simulator intensity was performed with a Molelectron PS19 thermopile detector and a Molelectron PM500AD power meter to satisfy the AM1.5 (1000 Wm\(^{-2}\)) intensity.

The devices were exposed with light under the sun simulator and the electrical characteristics were acquired performing a voltage sweep while measuring the output current with the source-meter (Figure 4-7). Labview software was used to control the Keithley instrument and to record the electrical measurements.
4.3.2 Solar cells spectrum response

The spectral response of solar cells known as the External Quantum Efficiency (EQE) was measured with standard lock-in technique according to IEC60904-8 (1998). The EQE represents the number of incident photons per wavelength which are converted to electrons and extracted successfully out of the photovoltaic device.

The characterization was performed with a PVE300 photovoltaic device characterization system from Bentham Instruments. The system employs two light sources; a Xenon lamp which provides high output in the visible range and a quartz halogen lamp provide a stable output light for wavelengths up to 3μm. The light traverses a monochromator for wavelength selection and passes into a second monochromator for minimizing possible scattered light from the walls and structures.
within the monochromator which it can impose adjustments in the intensity of the signal. The monochromatic beam is modulated with an optical chopper and collimated onto the sample. A third quartz halogen lamp fitted with an AM1.5G filter is used to provide bias light for the solar cell under characterization. The modulated current produced by the sample cell is driven through a transform into a standard lock-in amplifier for demodulation and accurate estimation of the EQE. The lock-in amplifier is used to overcome the low level detection limits of solar cell device (detector) as well as improve the signal-to-noise ration. For calibration a silicon photo-detector from Newport and a reference spectral response curve provided by Bentham were used.

### 4.3.3 Conductivity measurements

To determine the resistivity of the laser annealed ITO substrates a four probe station from Jandel (Model RM3) was used to measure the films’ sheet resistance. The sheet resistance for a film can be estimated using the voltage-current measurements according to

\[
R_{sh} = 4.53(V/I)f_1f_2
\]  

*Equation 4-7*

The probe head which was used contained four probes separated by 1mm from each other.

The resistance between the laser structured interdigitated electrodes which were used for the sensing elements at chapter 7 was measured with a Keithley 2400 source-meter. A two probe configuration was used to acquire the voltage-current measurements and determine the resistance from Ohm’s law.
4.3.4 Capacitance measurements

A Keithley 595 quasistatic capacitance-voltage meter was employed to measure the capacitance between the interdigitated electrodes formed by laser annealing in chapter 7. The meter applies two different voltages \( V \) with a delay in the capacitive device and monitors the charge flow \( Q/t \) at the device between this two voltage transitions. The capacitance \( C \) is derived from those values with the following equation

\[
\Delta V = \Delta Q / C
\]

Equation 4-8

An internal feedback circuit is used to minimize the errors. The meter’s resolution can be programmed from 1fA up to 10nA according to the measuring range.
5 Metal nanoparticles fabrication and characterization using laser annealing

For any electrical device, be it a solar cell or sensor, where the nanoparticles (NPs) are going to be used, it is necessary to be able to reproducibly fabricate NPs in a controlled manner in order to achieve the desired enhancement. Among the different metal nanoparticle fabrication methods described in chapter 3, laser annealing is one of the most favourable, because it can meet the specifications for low cost, large area, readily to integrate in industrial processes such as roll-to-roll and without hazard waste. Although rapid laser annealing is an environmental friendly technique with lots of advantages due to its nature, there are not many studies which are using this technique to fabricate NPs in a controlled manner for use in active optoelectronic devices due to a concern about the ability to control the MNs dimensions and their quality. The following work demonstrates good controllability over size, inter-particle separation, surface plasmon resonance position and extinction tune-ability between forward scattering and absorption of light.

The process involves coating of the substrate with a thin metal film and rapidly laser annealing it with a Lambda-Physik LPX 210i Excimer KrF laser to form the nanoparticles. All substrates before any film deposition were cleaned by ultrasonic agitation for 10 min in acetone, isopropanol and methanol, sequentially. Metal nanoparticles made from Ag and Au were fabricated and studied in this work because they exhibit SPR and high scattering efficiencies within the solar spectrum. However other metals or composites including ITO[155], GaMg[156] and Cu[25] can
be used because they are also exhibit SPR in the visible-IR spectrum. The extinction of Ag particles is stronger compared to Au although silver is known to oxidize in air. Due to oxidation of Ag, one should expect that a thin layer of silver oxide forms over the particles’ surface, changing the surrounding dielectric medium and shifting the SPR position. However spectroscopic measurements of the same Ag nanoparticles over time did not show any changes in the SPR, which is a sign that Ag nanoparticles are stable over long period.

Over the course of this study for all sputtered metal films a JLS (MPS 500) sputter deposition system was used. The background pressure in the chamber prior to deposition was $1.2 \times 10^{-6}$ Torr and Argon (Ar) was used as sputtering gas under a pressure of 3.5 mTorr and flow rate of 25 sccm. While for all the metal films deposited through evaporation, a thermal evaporator was used. The average deposition rate for all materials was 0.1 - 0.2 Å/s and a pressure of $1.0 \times 10^{-6}$ Torr was maintained in the evaporation chamber during this process, unless otherwise stated.

5.1 Nanoparticles fabrication and characterization on plain glass substrates

Silver nanoparticles exhibit strong extinction efficiencies allowing better investigation of localized surface plasmons. Standard microscope glass slides were sputtered with 5nm silver. Deposition of such ultra thin films has been studied before under the Stranski-Krastanow and Volmer-Weber models[59]. The model proposes that the film grows epitaxial due to strong adatom-adatom interactions
forming first discontinuous islands, thereafter the islands grow forming porous films to end up in uniform metal films. Because sputtering involves high energetic atoms which collide on glass surface, high density uniform films are expected for this thickness verified by other studies[157].

The metalized glass substrates were laser annealed at different areas using different laser fluences of 40, 92, 190 and 273mJ cm\(^{-2}\) and scanning speed of 40mm/min to determine the influence of laser fluence on nanoparticles size. Metal nanoparticles were observed only for the fluences of 190 and 273mJ cm\(^{-2}\), where the metal film melted and due to surface tensions on the liquid metal, particles were formed with the mechanism elucidated in previous chapter. The morphology of samples was characterized by AFM to determine the size distribution. The annealed metal film areas at 190mJ cm\(^{-2}\) formed bridged relatively big particles, with spinodal morphology and wide size distribution from 1 to 25nm (Figure 5-1 a, e). The spinodal morphology indicates that the delivered energy is near the critical melting threshold imposing perforations in the film and big spinodal particles due to partial film melting. The root mean square (RMS) roughness of the film is 4.63nm and the average particle height is 12.85nm (Table 5-1). For higher laser fluences the sintering phase is complete, forming smaller particles dictated by the general rule where particles tend to settle in structures with a smaller volume[59]. This is supported by Figure 5-1 c, e where the film annealed at 273mJ cm\(^{-2}\) forming smaller particles with film RMS roughness 1.025nm and average particles height of 2.7nm. Concomitantly particles size can be tuned by selecting carefully the laser fluence. The 3D morphology reconstruction from AFM data, the RMS roughness, average height and
size distribution were analyzed using the WSxM 4.0 program form Nanotec Electronica.

Plasmonic devices such as solar cells are multilayer sandwiched structures with metal nanoparticles usually to be integrated in one of these layers which it can be conductive such as the front or back contact. To study the effect imposed by a conductive surrounding medium in metal nanoparticles SPR, 5nm of Al was evaporated on the initial Ag MNFs and characterized morphologically and optically in comparison with the uncoated Ag MNFs. The RMS roughness and average height for the film with the big bridged particles which were annealed at 190mJ cm⁻² were reduced to 4.37nm and 10.9nm respectively, indicating that the perforation areas and the spinodal endings on particles were covered with Al creating a smoother surface (Figure 5-1 b). Vice versa at the 273mJ cm⁻² annealed film with small particles the RMS roughness and average height were increased to 1.31nm and 3.69nm respectively. This could be explained by the epitaxial deposition of Al on top of uniform shaped small particles leading to increased particles’ height (Figure 5-1 d). For both cases the size distribution is broadened slightly and smoothed (Figure 5-1 f). An analytically display of the different RMS roughness and average particles’ height versus Laser fluence is shown in Table 5-1.
Table 5-1 RMS roughness and average height of the features Ag for the different laser annealing fluences before and after Al coating.

<table>
<thead>
<tr>
<th></th>
<th>Ag particles</th>
<th>Ag particles covered with 5nm Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMS Roughness in (nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>after irradiation at 190 mJ cm$^{-2}$</td>
<td>4.63</td>
<td>4.37</td>
</tr>
<tr>
<td>Average height in (nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>after irradiation at 190 mJ cm$^{-2}$</td>
<td>12.85</td>
<td>10.9</td>
</tr>
<tr>
<td>RMS Roughness in (nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>after irradiation at 273 mJ cm$^{-2}$</td>
<td>1.025</td>
<td>1.31</td>
</tr>
<tr>
<td>Average height in (nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>after irradiation at 273 mJ cm$^{-2}$</td>
<td>2.7</td>
<td>3.69</td>
</tr>
</tbody>
</table>
Figure 5-1 AFM images and their 3D spatial representation of Ag nanoparticles annealed at a) 190mJ cm\(^{-2}\) c) 230mJ cm\(^{-2}\) and the same films after coated with 10nm Al b) 190mJ cm\(^{-2}\) and d) 230mJ cm\(^{-2}\). e) shows the particle size distribution for the two different laser fluences and f) the size distribution after evaporating 5nm Al on top of initial MNFs. The scale bars for each image are a), b) 30nm, c) 10nm d) 15nm.
A Cary 5000 spectrometer was used to acquire the optical signature of MNFs where the characteristic plasmonic peak was observed.

![Graph](image)

**Figure 5-2** Optical signature of MNFs before and after burring them with 5nm Al a) annealed at 190mJ cm\(^{-2}\) and b) annealed at 273mJ cm\(^{-2}\).

For both annealed areas at 190mJ cm\(^{-2}\) and 273mJ cm\(^{-2}\) a strong absorption was observed across the wavelengths 350nm to 650nm due to Ag nanoparticles with the SPR peak at 455nm (Figure 5-2 b). The Full width half maximum (FWHM) for the 190mJ cm\(^{-2}\) is 120nm, relatively wide imposed from the wide number of particles distribution size (Figure 5-1 e). On the other hand, the FWHM for the 273mJ cm\(^{-2}\) is 90nm creating a sharper shape with enhanced absorption. Capping nanoparticles with an addition thin Al film of 5nm and measuring again the optical signature revealed that the characteristic SPR absorption peak still existed. However, the peak absorption point decreased by 0.268 units for the 190mJ cm\(^{-2}\) and 0.259 units for the 273mJ cm\(^{-2}\) and the peak position blue shifted to 387nm and 393nm, respectively. A possible explanation for the blue shift is that the extra Al film alters the dielectric constant around the nanoparticles in a way that the SPR shifts to the blue side based on Equation 2-17. A theoretical model based on a simplified structure of one core-shell particle is displayed in Figure 5-3 confirming that assumption. In the simulation
tool [158] the core was set to 10nm Ag, the shell 5nm Al with refractive index at 455nm 0.65083 [159] and the surrounding medium modelled as glass material.

![Extinction simulation](image)

*Figure 5-3 Extinction simulation for 10nm Ag single nanoparticle on glass and 10nm Ag covered with 5nm Al core-cell nanoparticle on glass.*

On the basis of simulation data, the dielectric constant of the surrounding medium has a stronger impact on the modulation of SPR peak compared to the particles’ size. This is of great importance because any MNF can be tuned by capping the metal nanoparticles with a surrounding medium of appropriate dielectric constant. Furthermore, the suppression of absorption and the shift of the extinction curve at values below zero (compared to films with no Al coating), especially in the MNF with bigger nanoparticles, is the indication that forward scattering is higher in the Al buried films compared to plain Ag particles, which is a very important feature for plasmonically enhanced photovoltaic cells.
5.2 Nanoparticles fabrication and characterization from evaporated metal on ITO coated glass substrates

Conductive indium tin oxide (ITO) substrates with integrated metal nanoparticles for plasmonic effects are attracting considerable attention in the fields of solar cells[24, 40, 160], light emitting diodes[161], optical filters[82], Raman sensors[13, 144, 148] and gas sensors[14], due to the enhancement in light coupling efficiency between the surface plasmons (SP) developed at the nanoparticles surface and the device[162]. These novel architectures offer many more options to design more optimized structures with specific light management. Although methods to create metal particles are in abundance, it is generally challenging and difficult to produce a single step process that enables one to print accurate plasmonic structures and secondly, to tune their surface plasmon resonance (SPR) to the required specifications.

Commercial pre-patterned ITO special glass substrates acquired from the Lumtec company were covered with 5nm of Ag or Au by slow (0.2~0.3 Å/sec) thermal evaporation and annealed at 50mJ cm\(^{-2}\), forming successfully metal nanoparticles in both cases (Figure 5-4 a, b). The low power was used to minimize the thermal damage incurred on the ITO beneath, since high fluence laser annealing is known to degrade the quality of ITO film by lowering the oxygen vacancies and thus reducing its conductivity[91]. The annealing process formed particles with a wide range of size distribution typically between 2 to 65nm for both metals. The majority of Ag particles were 15nm while for the Au particles 23nm as AFM analysis shows in Figure 5-4 c. That relatively wide range of particles sizes is attributed first to the deposition
method where deposited metal films have lower adhesion with the substrate as well as lower density compared to sputtered films where the highly energetic metal atoms penetrate into the substrate up to a specific level. Secondly, the morphology of ITO and its surface interaction with Ag and Au determined the wet-ability. The broad spread shape of absorption for both metals displayed in Figure 5-4 d, is a characteristic imposed by the wide range of particles sizes, where the SPR of different size particles is at nearby frequencies and their superposition forms the final shape. The absorption peak for Ag particles is at 545nm and for Au at 600nm. The red shift of Ag peak compared to particles on plain glass results from the bigger size and the higher refractive index of ITO (2.03) compared to glass (1.68 for BAF10 at 455nm), agreeing well with theory.

Figure 5-4 Metal nanoparticles on top of ITO using 50mJ cm⁻² fabricated from a) Ag, b) Au with scale bars 105 and 175nm respectively, c) is their size distribution and d) their optical SPR signature.
The SEM images illustrated in Figure 5-5 show clear evidence that the annealed ITO films are damaged even at that low laser fluence (50mJ cm$^{-2}$). Cracks on the surface of ITO films are formed after laser annealing at 50mJ cm$^{-2}$ in both cases of Au and Ag coating. These cracks on ITO surface degrade the quality of the film imposing changes to its conductivity. This makes apparent the necessity for use of a sacrificial layer on top of ITO to prevent degradation of conductivity for possible use of this technique in applications such as polymer solar cells where the contacts resistivity is a crucial factor, determining the device efficiency through their series resistance.

![SEM images of a) gold and b) silver nanoparticles formed on ITO after annealing the evaporated films at 50mJ cm$^{-2}$. The scale bars for each picture are 500nm.](image)

The electrical resistivity of ITO annealed at 50mJ cm$^{-2}$ increased $\sim$1.6ohm/□ compared to untreated samples. A more in-depth analysis on the effects of laser annealing on electrical resistivity of ITO is presented in the following section.
5.3 Nanoparticles fabrication and characterization from sputtered metal on ITO coated glass substrates

Indium Tin oxide (ITO) is the most commonly used material as front contact in organic based solar cells. One of the major difficulties in device fabrication is the production of uniform metal nanoparticle films (MNFs) over large area substrates and the repeatable tuning of their SPR in one step. Due to high importance of metal nanoparticles fabrication on ITO, an in depth characterization of the metal nanoparticles fabrication on ITO were performed with different laser powers. Figure 5-6 illustrates graphically the effects of laser annealing Au-ITO coated substrates. The actual laser annealed samples are illustrated at Figure 5-7. The physical properties of the treated ITO film such as electrical conductivity, opacity, surface morphology and position of localized surface plasmon resonance wavelength are studied and theoretically modelled.

![Figure 5-6 graphical representation of the laser annealing process at different laser powers for Au metal nanoparticles fabrication on ITO. The different colours at metal nanoparticles represent the shift of metal nanoparticles SPR peak at each path, when annealed at different laser fluences. The shift in the particle’s SPR](image)

95
is imposed from the change of the dielectric constant value in the surrounding medium (ITO) during the laser processing. Different laser fluences impose different changes in the surrounding medium’s dielectric constant resulting in different intriguing colours.

Plain Corning glass and Corning glass coated with 130nm ITO acquired from a commercial supplier were sputtered with 5nm of 99.99% pure gold. The samples were mounted on a computer controlled translation stage moving at a typical speed of 50mm min⁻¹, and annealed at different laser fluences. For the electrical characterization a four probe station from Jandel (Model RM3) was used to measure the sheet resistance of the laser annealed areas. A probe head with 1mm separation distance between each probe were used for the electrical measurements.

Once the samples were laser annealed, a strong change in colour was observed, as shown in Figure 5-7 a). This colour changes is attributed to the generation of metal particles with SPR absorption in the visible regime. For the plain glass substrate only one colour was observed for all the different laser fluences which formed MNs. A minimum laser flux of 110mJ cm⁻² is required prior to transform the thin metal film to metal nanoparticles on the plain glass substrate.

For the ITO coated glass substrate, different profound colours are observed for each different laser fluence, (Figure 5-7 a) on indication that MNs are formed and their SPR can be tuned by adjusting only the power of laser. Programming the translation stage with different unique patterns and then applying different laser fluences, several multicolour plasmonic images were printed (Figure 5-7 b-d), demonstrating the versatility and robustness of the technique for industrial printers to fabricate unpolarized conductive substrates with spectral response within the visible regime suitable for bespoke optoelectronic devices. Furthermore, this technique can be
used to print photonic circuits[163] with specialized properties such as integrated optical demodulators whereby controlling the laser power, optical paths with different wavelength responses to spatially dispersed light [164] can be fabricated without the need or requirement of expensive lithography.

Figure 5-7 a) Real image of the laser irradiated paths with different laser fluencies on Au/glass b) Au/ITO/glass substrates and their impact on their SPR c) the flag of Advanced Technology Institute (ATI) in 3D printed using three distinct laser fluences, d) flag based on 5nm Au initial film and e) flag with 5nm Ag initial film printed with this technique.

One single characteristic plasmonic peak at 524nm was exhibited from all areas on plain glass which were annealed at fluences above 110mJ cm\(^{-2}\) (Figure 5-8 a). The resonance around 524nm is consistent with the SPR wavelength of Au particles on glass, indicative of homogenous size nanoparticles formation.
Figure 5-8 Optical characterization of laser annealed at different fluencies Au film a) on plain glass b) on 130nm ITO coated glass.

The ensembled optical spectra of all laser thermo-graphically printed patterns on ITO at different fluences are shown if Figure 5-8 b. Intriguing is the change of SPR wavelength and shape ensuing from the laser fluence variation. All SPR wavelengths appear around 500nm to 650nm. The extinction values below zero which are
displayed at Figure 5-9 for wavelengths above 650nm denotes that forward scattering takes place in the nanostructured areas.

At 44mJ cm\(^{-2}\) where the first SPR peak appears at a wavelength of 577nm denotes the approximate threshold fluence for metal nanoparticles fabrication on ITO. This difference in threshold energy compared to glass is related firstly with the higher absorption coefficient of ITO at 248nm laser wavelength which results in increase surface heating and secondly with the different values of the enthalpy for nanoparticles formation between the ITO/Au and Glass/Au films[21]. For a material compound in steady state, enthalpy of melting denotes the energy required to change the state from solid to liquid of one mole of this material compound. In our system different laser input energies are required for the two substrates, due to additional energy required to heat the glass substrate. For the bilayer structure ITO/Au for the process making particles the enthalpy is relatively lower compared to the glass/Au bilayer structure due to different physical properties of the glass and
ITO, such as thermal conductivity, heat capacity, mass density and light reflectivity at 248nm.

Increasing the power, the plasmon resonance shifts towards infra red (IR) frequencies (Table 5-2) up to 591nm at 72mJ cm$^{-2}$ where there, it appears to be a second energy threshold. For fluences up to 70mJ cm$^{-2}$ no variation of particles’ size were denoted in SEM images (Figure 5-10 b, c, d), thus the red shift must be associated with the change in dielectric properties of the ITO ensuing from the different annealing energies [165, 166]. That concept is further elucidated in the following sections. At 72mJ cm$^{-2}$ the SPR red shift it is relatively small compared to the sudden increase in sheet resistance to 590 ohm/□. The average size of NPs at this fluence is decreased to 13nm, which theoretically should induce a blue shift, therefore that relatively small SPR shift can be explained by the simultaneous occurrence of two processes with opposite effect on the SPR wavelength and their net effect is to induce only a small shift.

For higher fluencies the SPR shift backwards to shorter wavelengths. For the energy flux of 102.6mJ cm$^{-2}$ the SPR appears at 584nm and for just an 8mJ cm$^{-2}$ higher fluence the resonance moves to 551nm while the absorption over the entire visible spectrum increases rapidly. That blue shift can be associated with the decreased size of particles and their partially embedding within the ITO.

For fluences above 141.3mJ cm$^{-2}$ the ITO totally melts and is no longer continuous after solidification. The absorption increases throughout the spectrum and dominates over the characteristic plasmonic signatures. This exaggerated absorption
can be attributed to the big ITO ribbons, which formed during the initial film melt. These big ITO grains increase the omnidirectional scattering at these areas.

Table 5-2 details of laser fluence, electrical resistance of the annealed areas, free carriers density, SPR peak wavelength and nanoparticles formation.

<table>
<thead>
<tr>
<th>ID from Figure 5-7</th>
<th>Laser fluence (mJ.cm⁻²)</th>
<th>Sheet resistance (ohm/□)</th>
<th>Free carrier density (cm⁻³)</th>
<th>SPR wavelength (nm)</th>
<th>NPs average size (nm) from SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA</td>
<td>0</td>
<td>15.7</td>
<td>2.11x10²¹</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>(i)</td>
<td>34.6</td>
<td>15.1</td>
<td>2.19x10²¹</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>(ii)</td>
<td>44</td>
<td>16.2</td>
<td>2.03x10²¹</td>
<td>578</td>
<td>29±4</td>
</tr>
<tr>
<td>(iii)</td>
<td>50.6</td>
<td>17.1</td>
<td>1.94x10²¹</td>
<td>581</td>
<td>29±4</td>
</tr>
<tr>
<td>(iv)</td>
<td>70.6</td>
<td>18.5</td>
<td>1.79x10²¹</td>
<td>588</td>
<td>29±4</td>
</tr>
<tr>
<td>(v)</td>
<td>72</td>
<td>590.3</td>
<td>5.6x10¹⁹</td>
<td>590</td>
<td>13±2</td>
</tr>
<tr>
<td>(vi)</td>
<td>102.6</td>
<td>71.5x10³</td>
<td>4.63x10¹⁷</td>
<td>584</td>
<td>13±2</td>
</tr>
<tr>
<td>(vii)</td>
<td>110.6</td>
<td>1.2x10⁶</td>
<td>2.85x10¹⁶</td>
<td>551</td>
<td>13±2</td>
</tr>
<tr>
<td>(viii)</td>
<td>141.3</td>
<td>1.5x10⁷</td>
<td>2.22x10¹⁵</td>
<td>547</td>
<td>13±2 Embed</td>
</tr>
<tr>
<td>(x)</td>
<td>160</td>
<td>No conductive</td>
<td>NA</td>
<td>(Hidden)</td>
<td>54±6 Embed</td>
</tr>
<tr>
<td>(ix)</td>
<td>221.3</td>
<td>No conductive</td>
<td>NA</td>
<td>(Hidden)</td>
<td>54±6 Embed</td>
</tr>
</tbody>
</table>

Figure 5-10) displays SEM images of the laser nanostructured surfaces for both, ITO coated and plain glass substrates. The particles’ average size on ITO are the same 29±4nm independent of the laser fluence for fluencies up to 72mJ cm⁻² agreeing well with other studies[21, 86, 167] which report that diameter of nanoparticles is proportional to the initial metal film thickness. For energy densities between 102.6mJ cm⁻² and 141.3mJ cm⁻² the extra energy delivered per pulse allows the formation of metal grains with higher surface energy forming NPs with smaller average size of 13nm diameter. For higher fluences the excess heat coupled to the metal NPs and ITO totally melts them, elongating the cool down period. This allows
extra time for the aggregation process with bigger Au particles to be formed at approximately 54nm diameter (Figure 5-10 i-k) which are embedded in big isolated ITO ribbons.

On glass substrate the different morphology, thermal conductivity and free enthalpy between glass surface and Au film induce different fragmentation dynamics compared to ITO which allow the particles' formation at fluences only above 102.6mJ cm$^{-2}$, with smaller diameter of 13nm (Figure 5-10 l).

![Figure 5-10 SEM images acquired from the 5nm Au / 130nm ITO coated substrate for all different laser fluencies](image)

Indium Tin Oxide is a degenerate n-type semiconductor[168] whose its conductivity is primarily related to the quantity of oxygen vacancies in the film[169]. Laser annealing alters the quantity of O$_2$ vacancies in the ITO film by dissociation [166, 170, 171] influencing its electrical properties. Furthermore, when increasing the irradiation power, cracks are induced in ITO film which further degraded its conductivity (Figure 5-10 b-g). Figure 5-11 displays the film resistance versus laser fluence. The film resistance calculation performed using four probes IV
measurements and Equation 5-1 with corrections factors $f_1=f_2=1$ due to the very small thickness of ITO (130nm) compared to probe separation distance (1mm). 

$$R_{sht} = 4.53(V/I)f_1f_2$$  \hspace{1cm} \text{Equation 5-1} \\

Figure 5-11 Sheet resistance measured with a four probe source-meter versus laser fluence

For low fluencies up to 70mJ cm\(^{-2}\) the sheet resistance increases relatively proportionally to the delivered power. That increase is associated with the dissociation of oxygen vacancies near the surface of ITO [166, 170]. The sudden increase of sheet resistance at 70mJ cm\(^{-2}\) is associated with the degradation of ITO crystal structure near the surface which the thermal shocks are imposed[91]. Beyond that fluence it is clear in SEM images the degradation of crystal structure where big cracks appear across the film increasing exponentially the resistance.
5.3.1 Theoretical modelling of Au surface plasmon resonance shift on ITO

In this section a theoretical investigation is undertaken in order to elaborate the SPR shift which occurs with laser annealing at different fluences. The SPR shift could be imposed by three different mechanisms based on the main observations. First it could be due to different resistivity values of ITO after laser annealing. Second the SPR shift could be attributed to the change of particles’ size, although the size changes only at high fluencies. Third, the laser annealing could modify the stoichiometry of ITO film producing individual elements of Tin (Sn) and Indium (In) with different dielectric constant affecting the particles’ SPR. Due to the semiconducting nature of ITO it is possible to use classical semiconducting theory and the Drude model to calculate its electrical and optical properties.

For the first assumption, ITO resistivity is related to the concentration of free carriers $N$. Thus the density of free carriers can be estimated from resistivity using Equation 5-2 under the assumption that electron mobility of ITO is $\mu_e=14.5$ cm$^2$ V$^{-1}$s$^{-1}$ and constant throughout the film[172].

$$\rho = (eN\mu_e)^{-1}$$

where $e$ is the charge for a single electron and $\mu_e$ the mobility of electrons in the film.

The resistivity deduced from the real values of sheet resistance using 130nm for the ITO film thickness, as to the real sample.

The density of free carriers for the untreated areas estimated to be $2.11\times10^{21}$ cm$^{-3}$ which agrees with other studies [166, 172]. The number of free carries decreases
proportionally with the resistivity of ITO film, to be 6 orders of magnitude lower for the area annealed at 141.3mJ cm$^{-2}$ with sheet resistance 14.875Mohm/□.

Figure 5-12 illustrates the density of free carriers for all the laser fluences which produced conductive patterns and the measured SPR wavelength for each case.

![Figure 5-12 Number of free carriers versus laser fluence and their association with the measured SPR wavelength](image)

Changes in the density of free carriers in ITO films by altering the concentration of oxygen vacancies induce variations to its dielectric constant and refractive index[172]. One can expect that incorporating metal nanoparticles which exhibit plasmonic resonance in ITO films and manipulating the concentration of oxygen vacancies should shift SPR. Concomitantly, the SPR variation in laser annealed ITO coated substrates may be attributed to the conductivity change in the ITO film. For the experiment all sputtered gold films which were used, were pure Au (99.99%). Therefore the electric permittivity $\varepsilon_{Au}$ should be constant for all fabricated metal nanoparticles with similar size. Concomitantly, the SPR shift on the annealed areas at
ITO coated samples should be attributed mainly to variations in the surrounding medium permittivity $\varepsilon_{ITO}$.

Decrease in free carriers’ density increases the relative permittivity $\varepsilon_{ITO}$. One should expect a red shift in SPR according to quasi static approximation solutions for particles extinction in chapter 2. This concept agrees with the data in Figure 5-12 for fluences up to 72mJ cm$^{-2}$; above this point blue shift occurs in the real sample, indicating the involvement of a second process.

The ITO permittivity dispersion modified by changing the number of free carriers and the Au permittivity were calculated using the Drude approximation from Equation 2-1 and Equation 2-2. For the calculations of ITO plasma frequency $\omega_p$, the densities of free carriers based on the real measurements in Figure 5-12 were used.

Figure 5-13 displays the real and imaginary parts of Au and ITO relative permittivity. For the calculations the following parameters were used Au $\varepsilon_{int(Au)}=6.9$, $\omega_{p(Au)}=8.9$ (eV), $\gamma_{(Au)}=0.07$(eV) [173] and for ITO effective mass $m_{ITO}^*=0.4m_e$, mean relaxation time $\tau_{(ITO)}=5\times10^{-15}$ s [165] and $\varepsilon_{int(ITO)}=4.55$ [172].
Figure 5-13 Modeled relative permittivity dispersions of ITO modified by altering the number of free carriers a) real part b) imaginary part c) the real part of Au permittivity and d) the imaginary part of Au.

The calculated values of relative permittivity agree well with other studies for both ITO [168, 172] and Au [30].

A decrease in the concentration of carriers has an opposite impact on the relative permittivity $\varepsilon_{ITO}$ of ITO inducing increase at the real part of dielectric constant. The increase in real part of dielectric constant is more profound at long wavelengths near the plasmonic resonance wavelength of Au. Thus strong red shifts should take place as has been observed in real samples. At carrier concentrations below $5.609 \times 10^{19}$ cm$^{-3}$ which are associated with laser fluences above 72 mJ cm$^{-2}$, the real part of dielectric constant increases rapidly and remain constant throughout the visible spectrum. Hence any variation in carriers’ concentration below $10^{19}$ cm$^{-3}$ it should
not affect theoretically the SPR wavelength of Au nanoparticles in the visible spectrum.

The extinction for a metal nanoparticle is primarily influenced by the dielectric constant $\varepsilon_a$ of the surrounding medium and the metal nanoparticle complex dielectric constant $\varepsilon_m = \varepsilon_{m(\text{re})} + i\varepsilon_{m(\text{im})}$ according to Mie solutions for spherical particles [1, 174]. The extinctions dispersions were calculated (Figure 5-14) with a custom made program in Matlab based Equation 2-17 and the assumption that the surrounding medium is only ITO. Although the ITO’s dielectric constant $\varepsilon_{ITO}$ is a complex number for the simulations only the real part was used.

![Figure 5-14 Simulations of Au nanoparticle extinction in ITO for different laser fluences](image)

The best approximated fit with the real SPR wavelengths for a single value of initial dielectric parameter $\varepsilon_{\text{int}}$ were acquired at $\varepsilon_{\text{int}}=6.5$, and displayed in Figure 5-14 with solid lines. The main reason for the deviation of theoretical values in comparison
with the real ones is the assumptions which we used for the theoretical calculations. In the model the assumption that the Au particles are surrounded totally by ITO was used. However, in the real sample the annealed areas with low laser power, the particles are mainly surrounded by air and only a portion of the particles surface at the bottom is interfacing with the ITO. Despite the simplicity of the model a useful outcome was extracted about the mechanism of SPR tuning. The Au particle’s SPR wavelength red shifts as the laser power increases until the threshold power of 72mJcm\(^{-2}\), which is similar to the real measurements. This shift occurs due to the increase of the ITO’s relative permittivity as was mentioned before.

The SPR wavelength remains constant for higher fluence as it was expected, since the relative permittivity is relatively constant in the visible regime for all carriers’ concentrations below \(10^{19}\) cm\(^{-3}\). The derived simulation data denote that the size of particles primarily influencing the amplitude of extinction and slightly its position, concomitantly the initial notion that blue shift yield from the decreased particles size at high fluences is controversial since such a big blue shift cannot match with the observed size reduction. Furthermore studies from other groups indicate that partially embedding particles into a medium with a refractive index higher than vacuum should cause a red shift [2]. The simulated curves which fit well to the real extinction measurements of blue shifted SPR signatures were performed using lower values than \(\varepsilon_{int}=6.5\), as displayed in Figure 5-14 with dashed lines. The initial dielectric parameter is inversely related with the ITO’s relative permittivity, thus blue shift should occur for lower \(\varepsilon_{ITO}\) values.
Annealing ITO at high fluences damages the crystal structure of ITO and removes oxygen from the film [91]. Intuitively a possible explanation is that the stoichiometry changes after annealing at very high temperatures which cause melting, affecting the dielectric constant in the remaining In$_2$O$_3$-SnO$_2$ structure. The new structure may have a lower dielectric constant and refractive index which is a notion which seems to agree well with other studies [175]. Thus, a blue shift in SPR for annealed areas at high fluences can be suggested.

5.4 Summary

Summarizing, metal nanoparticles fabrication and tuning of their surface plasmon resonance was been demonstrated on different materials.

- The experimental work, which was verified by theoretical modelling, shows there is an intimate relation between the resistance of the film and the SPR of the metal nanoparticles.
- Laser annealing the ITO causes variation in the O$_2$ vacancies near the surface of the film [170, 171] altering its resistance. Hence, this changes the nanoparticles’ SPR and colour at the irradiated areas.
- An increase of the ITO resistance at annealed areas compared to the untreated areas were observed, therefore a sacrificial layer on the interface could be beneficial to minimize the degradation.

This method can be used to fabricate conductive plasmon active substrates for solar cells or light emitting diodes using only low laser power to minimize damage and to keep good conductivity.
6 Laser nanostructured substrates for plasmonic solar cells.

Thin film polymer photovoltaics are attracting significant interest mainly due to their potential for manufacturing using low cost processes such as roll to roll, their mechanical flexibility, light weight which is ideal for portable applications, and their relatively high power conversion efficiencies comparable with a-Si:H. Despite all those advantages, thin film devices suffer from inefficient light absorption. The small thickness of the active layer, which is, required in organic based solar cells to maintain good charge transport and extraction[103] reduces the efficiency of photon absorption. Furthermore, another common problem which limits the efficiency for all types of photovoltaic cells is the limited utilization of the entire AM1.5 spectrum, a limitation which arises from the material properties such as the small band gap of the photo-active material. It has been demonstrated that structuring the front surface with small pyramids of μm height, the efficiency can be enhanced up to $4n^2$ where $n$ is the refractive index of the absorbing material, by scattering light into different angles and thus increasing the absorption path[176]. However, this approach is difficult to utilise in thin films where the overall active layer thickness is a few tens of nm. In addition, structuring does not allow the utilization of wavelengths which are not directly absorbed in the active material. These unabsorbed light wavelengths can cause thermal effects at the back and front contact, by exiting phonons where upon their relaxation, the temperature of the device increases. This thermal effect may lead to extra degradation in efficiency and life time if no precautions are taken, an aspect which can add extra cost. Incorporation of metal nanoparticles with sizes smaller than the wavelengths of light in the AM1.5 spectrum
to create and utilize surface plasmons or trap the light into the photonic devices[164] is an alternative promising solution[24]. It has been proven that the high contrast between the refractive index of metal nanoparticles and the surrounding medium works like very fine waveguides coupling efficiently the light (forward scattering) into the absorber[40]. Furthermore the strong local electric field of the surface plasmons can enhance the exciton dissociation in organic photovoltaics contributing positively towards power conversion[109]. In this chapter Au or Ag nanoparticles are fabricated on a polymer based buffer layer on top of ITO to minimize damage from laser annealing in order to build plasmonic solar cells. Control of the particles’ size and their density in the film were achieved and their effect on the power conversion efficiency is examined. Au based nanoparticles of particular size and spatial distribution polymer films enhance the device’s efficiency. Furthermore based on the findings, design considerations for utilizing the entire AM1.5 spectrum with plasmonic effects and enhancing the efficiency of polymer solar cells are discussed.

6.1 Buffer layer for minimizing damages during laser annealing

In Chapter 5 it has been shown that metal nanoparticles can be successfully fabricated on ITO which is mainly used as a front contact in solar cells. However, laser irradiation of ITO affected the quality of the film and its conductivity, which affects the series resistance $R_s$ of the device, a crucial parameter for efficient solar cells.
To mitigate that problem and maintain a good quality of the ITO film, a buffer layer of Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate) (PEDOT:PSS) on top of the ITO was introduced. PEDOT:PSS is normally used as a transparent electron blocking layer at the front contact of polymer solar cells. Hence the use of PEDOT:PSS as thermal buffer during laser annealing should not impose any electrical problem in the solar cell structure.

To determine the energy absorption at 248nm in PEDOT:PSS a UV transparent plain quartz substrate and a quartz substrate coated with 35nm PEDOT:PSS was used. The samples placed on a thermopile detector (Figure 6-1) from Coherent Ltd (1/4-20 M6) and laser irradiated at 54.1mJ cm\(^{-2}\).

![Experimental setup to measure percentage of energy absorption](image)

Figure 6-1 Experimental setup to measure percentage of energy absorption a) at plain quartz b) at quartz coated with 35nm PEDOT:PSS.

The intensity of light at the bottom of the substrates were 50.2mJ cm\(^{-2}\) for the plain substrate and 41.5mJ cm\(^{-2}\) for the PEDOT:PSS coated substrate. Thus a 17.3% reduction of light intensity takes place in the 35nm of PEDOT:PSS layer. Comparing with the findings from Chapter 5.3, irradiation at 50.2mJ cm\(^{-2}\) fluence is adequate to form metal nanoparticles on the surface of PEDOT:PSS, while under the assumption
that ITO will be below PEDOT:PSS the reduced fluence of 41.5mJ cm$^2$ is low enough to avoid ITO damage.

The conductivity of laser irradiated PEDOT:PSS film is maintained, a more detailed analysis of which is presented in the following section.

6.2 Polymer photovoltaics with plasmonic structures

When a thin metal film is laser irradiated at the proper fluence metal nanoparticles are formed [177, 178]. Herein it is demonstrated that the method can be used for fabricating and depositing simultaneously metal nanoparticles on top of polymers. For very short light pulses (ns) the annealing and cooling transient periods are very fast due to the short lifetime of the phonon's relaxation[82]. These very short times imply that the induced thermal effects are localized only at the surface of the irradiated area. Thus this method allows the fabrication of metal nanoparticles directly onto substrates made of temperature sensitive materials such as polymers without substantially damaging their physical properties.

6.2.1 Material and Methods

ITO coated glass substrates were initially cleaned by ultrasonication in water, acetone and isopropyl alcohol for 10min respectively, and subsequently blow dried with nitrogen. A five minute oxygen plasma treatment was used to clean small particles and enhance the ITO electrical properties[179]. PEDOT:PSS from Baytron was spin cast on top to form the first layer with a thickness of 35nm. The substrates were annealed for 10min at 150 °C in air and transferred into a thermal evaporator for Au deposition. Four separate substrates were deposited with a thin gold layer
each one at different thickness ranging from 0.6, 1, 3 and 5nm with deposition rate of 0.2Å/sec. All substrates were then placed on a translation stage set to at a speed of 60mm/min where they were laser annealed in air with a 248 nm KrF Excimer pulsed laser at the fluence of 50mJ/cm², and running at a repetition rate of 20Hz to fabricate metal nanoparticles.

For the solar cells fabrication a second PEDOT:PSS layer was then applied by drop casting and spinning at 8500rpm on each substrate to create a thin film of ~8nm which was then annealed for 10min at 150 °C in air. The substrates was then transferred into a nitrogen filled glove box and solution with a blend of poly(3-hexylthiophene) (P3HT) : phenyl-c61-butyric acid methyl ester (PCBM) at 20mg:20mg analogy in 1ml of o-dichlorobenzene was spin casted on top of the second PEDOT:PSS layer. The film was dried at 120 °C for 10min and films of bathocuproine (BCP) (7nm) and Al (90nm) evaporated through a shadow mask to form the back contact. The overall solar cell structure is displayed in Figure 6-2.

Figure 6-2 Structure of polymer solar cells with plasmonic features.
The current-voltage (IV) characteristics were measured with a Keithley 2400 source-meter under AM 1.5 G using an Ariel solar simulator and irradiation intensity of 1000W/m². A calibration cell from Newport was used to calibrate the solar simulator intensity. The external quantum efficiency values were acquired with a Bentham PVE300 photovoltaic characterization system. The mobility of PEDOT:PSS with Au nanoparticles was measured using a PCB SPCB-01 Hall effect probe from ECOPIA. The SEM images and EDX spectrum acquired with a Quanta 200 F microscope from FEI. The photoluminescence (PL) of the samples was measured with a Cary Eclipse spectrometer from Varian exciting them with a beam at 570nm wavelength. For the Raman measurements a Renishaw micro-Raman 2000 system with a 782 nm laser at 4mW was used. A (50X) optical lens was used to focus the laser down to an approximately 1µm diameter spot. The detector integration time was set at 1sec and 50 accumulations at the same location were acquired to improve the signal-to-noise ratio.

6.2.2 Results

The SEM images show that metal nanoparticles were fabricated on top of PEDOT:PSS layer after laser irradiation at 50mJ/cm² for all Au films with thickness 0 (ref), 0.6, 1, 3, and 5nm respectively (Figure 6-3 a-e ). An EDX study on a representative film with initial Au thickness of 1nm revealed that particles on the substrates consisted of Au (Figure 6-3 b).
Figure 6-3 SEM images of Au nanoparticles on PEDOT:PSS fabricated by laser annealing different thicknesses of Au thin films, a) no metal (reference substrate), b) 0.6nm, c) 1nm, d) 3nm, e) 5nm, f) photograph of samples before active layer deposition, g) EDX analysis verifies Au existence.

Analyzing the films one can observe that the irradiated initial Au films of 0.6 and 1nm produced big particles with wide separation distances while for thicker Au films of 3 and 5nm, dense nanoparticle films with smaller size particles are produced. For thick metal films, the energy is mainly absorbed in the metal, breaking the initial film to small droplets where due to very short cooling time related with the phonon relaxation time[82] small particles are formed without any aggregation between them. Conversely in 0.6 and 1nm thin films due to smaller metal thickness, extra energy is absorbed in the underneath PEDOT:PSS layer raising its temperature. That accumulation of extra thermal energy in the substrate subsequently decreases the
cool down rate, allowing extra time for aggregation of small particles into bigger ones with longer spacing distances.

The PEDOT:PSS layer serves a dual functionality. First it serves as an electron blocking layer for organic solar cells in the active layer and secondly as a buffer layer to prevent ITO thermal damaged from the UV laser irradiation maintaining its good conductivity. Furthermore, a second thin layer was spin coated on top of the metal nanoparticle films (MNFs) to minimize the film roughness and to prevent recombination problems at the surface of metal nanoparticles. This extra film was kept very thin (~8nm) to minimize the degradation of surface plasmon induced localized electric field [110]. The appropriate thickness of that film was selected based on experimental results which are elucidated in the following section.

Figure 6-4 displays the SPR signature recorded during optical characterization for all substrates with different Au particles sizes. For large particle MNFs in Figure 6-3 b, c with 65nm and 45nm diameters, respectively, and wide spatial separation, the absorption is relatively low. The lower values at long wavelengths, which were recorded for MNF with 45nm particle diameters compared to the reference substrate (ITO coated glass with spin coated and annealed two PEDOT:PSS layers), it can be attributed to forward scattering, which is normally dominating in the extinction of particles with big diameters. Vice versa for dense MNFs with small diameter particles Figure 6-3 d, e of 22nm and 15nm, the absorption component in the particles’ extinction is prominent.
The assumption that the forward scattering at high wavelengths is stronger for MNFs with big particles while absorption is dominant at small particles is verified by a theoretical model (Figure 6-5). The scattering and absorption components of extinction were calculated with a simulation tool[158] considering a single Au particle with diameter equal to the real ones acquired from the SEM images for each different substrate. The model simulated the particles embedded in a dielectric medium with refractive index 1.53 similar to that of PEDOT:PSS [180].
Figure 6-5 Simulation of Au particles extinction components a) scattering and b) absorption for each different diameter assuming a surrounding medium of PEDOT:PSS.

For the active layer a blended mixture of P3HT:PCBM was spin coated onto the substrate followed by an evaporation deposition of thin BCP/Al films through a mask to form the back contact (Figure 6-2). The plasmonic cells and the reference were characterized under AM1.5G at 1000W/m² to determine their performance.

Figure 6-6 shows the J-V curves and the external quantum efficiency (EQE) for each cell. The samples with the relatively larger particles 65nm and 45nm diameter show an enhancement at short circuit current density compared to the reference cell (Figure 6-6 a). Having a careful analysis of the external quantum efficiency measurements displayed in Figure 6-6 b, the current density enhancement can be attributed to two parameters. First, the increased number of photons which penetrate into the active layer, due to enhanced forward scattering components, this increases the number of photo-generated electrons. This induces a characteristic peak near the surface plasmon resonance (630nm) of particles. Second, the better charge extraction and collection as a result of the higher mobility (Table 6-1) in particle doped PEDOT:PSS films can be seen in the EQE as a current enhancement through the entire photoactive spectrum of the P3HT:PCMB mixture.
In Table 6-1 a detailed analysis of the electrical characteristics for each different cell is shown. Enhancement of efficiency compared to the reference cell is observed for the MNFs with big particles and wide spread distances made from 0.6 and 1nm thick Au film. While for the dense particle films fabricated from 3 and 5nm Au films, decreased efficiency was recorded. Furthermore, incorporating into PEDOT:PSS
relatively big particles enhances the mobility of the film (Table 6-1) while for films with small particles the high sheet resistance of particles[24] decrease the mobility.

Table 6-1 Electrical characteristics for each different cell and the mobility of Au doped PEDOT:PSS layer for all substrates prior the active layer deposition.

<table>
<thead>
<tr>
<th>Particle size / Film thickness</th>
<th>Effic. (%) with ±8% error</th>
<th>Area (cm²)</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>PEDOT:PSS film mobility (cm²/V s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>65nm / 0.6nm Au</td>
<td>2.42</td>
<td>0.73</td>
<td>0.54</td>
<td>8.30</td>
<td>54.08</td>
<td>2.070E+01</td>
</tr>
<tr>
<td>45nm / 1nm Au</td>
<td>2.61</td>
<td>0.73</td>
<td>0.54</td>
<td>7.76</td>
<td>62.31</td>
<td>2.376E+01</td>
</tr>
<tr>
<td>22nm / 3nm Au</td>
<td>2.21</td>
<td>0.73</td>
<td>0.52</td>
<td>7.17</td>
<td>59.88</td>
<td>2.041E+01</td>
</tr>
<tr>
<td>15nm / 5nm Au</td>
<td>2.37</td>
<td>0.73</td>
<td>0.52</td>
<td>7.37</td>
<td>62.30</td>
<td>1.913E+01</td>
</tr>
<tr>
<td>Ref / 0nm Au</td>
<td>2.40</td>
<td>0.73</td>
<td>0.530</td>
<td>7.60</td>
<td>59.00</td>
<td>1.856E+01</td>
</tr>
</tbody>
</table>

The AM 1.5 solar simulator which was used for the measurements is a class B according to IEC 60904-9 classification with 5% error in light uniformity. Furthermore a 3% of calibration uncertainty due to the reference cell from Newport which was used for calibration has to be accounted for. Thus the total error in measurements can be accounted to be 8%. The difference in refractive index between the Au particles and PEDOT:PSS forms a wave guide[40] managing efficiently the incoming light. In addition the strong local electric field may enhance the exciton dissociation in the active layer which has been proven experimentally from other studies [104, 105, 181]. Theoretical studies show that forward scattering for films with bigger particles dominates over absorption [42].
The EQE curves in Figure 6-6 b show an enhancement throughout the spectrum of active layer for the cells with big particle diameters of 65 and 45nm and a peak near 630nm where the forward scattering is predicted (Figure 6-5 a). Therefore the enhancement can be attributed to two effects. First the increased mobility of PEDOT:PSS with big particles results in a lower $R_s$ allowing more efficient charge extraction and higher currents throughout the entire active spectrum. Second, the surface plasmon effect enhances the light intensity near 630nm due to the dominant forward scattering component. Hence the increased number of photons converted to electrons contributes positively in the overall cells’ current.

Vice versa, in dense particle films the absorption of light at metal nanoparticles near the surface plasmon resonance (SPR) dominates, inducing a strong local E-field. The exciton dissociation is better due to the stronger local field as the photoluminescence (PL) of the dense films indicate lower quenching (Figure 6-7), which agrees with other studies [117, 119]. However, a number of photons are absorbed in the metal nanoparticles to excite the SPR, reducing the number of photons entering in the active layer as the EQE curves for small particles indicate in Figure 6-6 b, affecting the total performance of the cells. Furthermore, the high density of particles with small separation distances induces a shadowing effect[40], undesirable for high efficiency photovoltaics.
Figure 6-7 Photoluminescence spectra for all cells in open circuit configuration, excited with a pump wavelength of 570 nm.

The PL study verifies that extra quenching occurs in all films with particles compared to the reference, which is a desirable effect for enhancing the short circuit current. The lower quenching in films with big particles strengthens the assumption that the power conversion enhancement is mainly due to the dominant scattering effect for the large particles (Figure 6-5) as well as from a small contribution of the SPR generated E-field for those substrates. Furthermore, the higher mobility at PEDOT:PSS films doped with big Au particles (Table 6-1) provides a better charge transportation mechanism minimising the current losses.

The higher quenching for dense NMFs of relatively small 15nm Au particles and the relatively higher generated current compared to the film with slightly bigger particles (22nm), is a consequence of the stronger SPR E-field at small particles where the absorption is dominating. However, the reduced photon flux which reaches the
active layer due to that absorption and shadowing effect from nanoparticles leads to reduced efficiencies.

A Raman study was performed to determine the crystallization levels in the active layer similar to other studies[154]. Since one would expect that the crystallization in the devices with higher amounts of metal in PEDOT:PSS may differ due to the extra heat capacity and higher thermal-conductivity from the extra metal, which could result in higher heat transfer during the cell annealing process to enhance the phase separation in the blended active layer. A 782nm laser was used as a probe light for the measurements. The wavelength of the probe light was chosen carefully to be as much as possible far away from the SPR to eliminate signal distortion from effects such as surface enhanced Raman spectroscopy.

![Raman Study](image)

**Figure 6-8** Shift for all photovoltaic cells acquired with a pump laser at 782nm.

The Raman signal for all different metal thickness was similar indicating that the crystallization and phase separation is similar for all substrates independent of the
metal nanoparticles size and density in the film. Thus it is suggested that the variations in power conversion efficiencies are purely from the optical and electromagnetic modes which metal nanoparticles exhibit.

Having demonstrated that metal nanoparticles can enhance or suppress the power conversion by interacting with the light, a further study was performed to determine their role in the recombination process of electrons and holes, a process which is critical to achieve the optimum power conversion.

It has been reported by different groups that plain metal particles on the front contact[60] or inside the active layer[182] of photovoltaic cells degraded their efficiency. This is an effect which causes confusion in the plasmonic solar community, since the local field from SPR degrades with distance, the smaller the distance of nanoparticles from the active layer the stronger the effect due to the surface plasmons should be.

Plasmonic substrates prepared as previously with the same initial metal film thickness of 5nm Ag were fabricated. After laser annealing, metal nanoparticles with an average size of 17nm where produced. The substrates were coated with a second PEDOT:PSS layer using different spin coating speeds of 5500, 6500, 7500 and 8500 rpm to achieve different thicknesses. Silver particles exhibit a stronger SPR field, hence the effect should be stronger. The absorption spectra for all substrates with different spin coating speeds for the second PEDOT:PSS layer are presented in Figure 6-9. As expected, the absorption in the substrate without the second PEDOT:PSS layer is lower compared to the films with the additional layer. Furthermore the particles in that layer are relatively closer to the active layer. Thus one would expect
that the lower absorption and the stronger effect from SPR E-field in the active layer due to absence of the second PEDOT:PSS layer should result in a higher performance.

![Graph](image)

**Figure 6-9** Absorption for all Ag based particles substrates with different 2nd PEDOT:PSS layer prior the active layer deposition.

The JV curves and EQE characteristics are presented in Figure 6-10 with a more detailed analysis of the electrical characteristics in Table 6-2. Interestingly, for the device with no second layer of PEDOT:PSS, the efficiency is lower compared with those who have the thin PEDOT:PSS second layer.

The film with the second thinnest PEDOT:PSS layer spun at 8500rpm gave the highest efficiency (Table 6-2). This sample has the best fill factor among the samples with the additional layer. Increasing the thickness of that layer damps the efficiency, indicating that the thickness of PEDOT:PSS is affecting both the fill factor of the solar cell and the effect of surface plasmon induced E-field at the active layer since the E-field degrades very fast with distance[110].
Figure 6-10 a) J-V characteristic for all cells with different thickness of PEDOT:PSS at the second layer, b) EQE characteristic for the same cells.

Analyzing more carefully the device structure, the active layer is a blend of two semiconducting materials, therefore in the front contact surface it is expected that both donor and acceptor materials coexist in the same layer (Figure 6-2). For a
device without a second PEDOT:PSS layer, although the surface Plasmon field enhances the exciton dissociation, for the areas where a metal nanoparticle is in the cross boundary of donor and acceptor material can act as an ohmic link between the two semiconducting materials. Thus it is expected that some holes and electrons will recombine on the metal nanoparticle’s surface reducing the output current. Vice versa at the devices with the second layer, the PEDOT:PSS acts as an electron block layer reducing the probability of an electron - hole recombination on metal NP’s surface. While a thickness of around 8nm for the 8500rpm layer is thin enough to allow the E-field from surface plasmon resonance to influence the exciton dissociation in the active layer.

Table 6-2 Electrical characteristics for all cells with and without a second layer of PEDOT:PSS, based on Ag plasmonic structures.

<table>
<thead>
<tr>
<th>Speed coating the 2nd PEDOT:PSS layer</th>
<th>Effic. (%) with ±8% error</th>
<th>Area (cm²)</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8500 rpm</td>
<td>1.22</td>
<td>0.73</td>
<td>0.48</td>
<td>6.68</td>
<td>38.23</td>
</tr>
<tr>
<td>7500 rpm</td>
<td>1.0</td>
<td>0.73</td>
<td>0.41</td>
<td>6.60</td>
<td>36.70</td>
</tr>
<tr>
<td>6500 rpm</td>
<td>0.93</td>
<td>0.73</td>
<td>0.40</td>
<td>6.81</td>
<td>34.20</td>
</tr>
<tr>
<td>5500 rpm</td>
<td>0.72</td>
<td>0.73</td>
<td>0.34</td>
<td>6.49</td>
<td>31.74</td>
</tr>
<tr>
<td>No 2nd layer</td>
<td>0.78</td>
<td>0.73</td>
<td>0.37</td>
<td>4.70</td>
<td>43.58</td>
</tr>
</tbody>
</table>

Similarly the total error in measurements can be accounted to 8% due to 5% error in light uniformity in the AM1.5 solar simulator and a further 3% error from calibration uncertainty in the reference cell.

PEDOT:PSS is an effective hole transporting layer in organic devices to the anode due to its high work function and high hole affinity (usually reported between 4.8 to
5.2eV) [183, 184]. This high work function allows the formation of an ohmic contact with the P3HT reducing any energy barriers at the ITO interface. The formation of this ohmic contact between the ITO and the HOMO level of P3HT, promotes the transport of holes. While, the relatively big energy difference between the LUMO level of P3HT and the work function of PEDOT:PSS makes the electrons’ transport less favourable, therefore acting as an electron block layer [184, 185]. The process is described more in-depth in references [183-185].

The lower efficiencies recorded for the Ag nanoparticles substrates can be attributed to two factors. First, the mismatched Fermi level of Ag 4.52-4.74eV compared to PEDOT:PSS 5.0eV and the HOMO level of P3HT 5.2eV can cause a charge trapping area due to energy levels’ misalignment (Figure 6-11). Secondly, the strong absorption of photons in the Ag particles results in a reduced number of photons which reach the active layer.

![Energy diagram of P3HT:PCBM solar cell with Ag nanoparticles between the two PEDOT:PSS layers.](image)

**Figure 6-11** Energy diagram of P3HT:PCBM solar cell with Ag nanoparticles between the two PEDOT:PSS layers.
6.3 Summary

Summarizing, it has been demonstrated experimentally that metal nanoparticles can be fabricated successfully on polymers with rapid laser annealing and they can be used for plasmonic enhancement at polymer solar cells.

Thin (0.6-1nm) initial Au metal films form relatively big particles 45-65nm with wide spatial distribution, while thicker (3-5nm) initial Au films produce dense MNFs with small diameter particles (15-22nm) after laser annealing.

Metal nanoparticles on the front contact of a polymer blended solar cell can enhance or suppress the efficiency of solar cells depending on the size of nanoparticles and their density in the film.

Big Au particles with wide separations enhance the efficiency of solar cells due to enhanced forward scattering verified theoretically, and the higher mobility of PEDOT:PSS film with incorporated big particles which provides more efficient charge extraction.

Small particles induce a stronger E-field as a consequence of the higher absorption. In devices with small particles, the stronger E-field enhances the fluorescence quenching as a PL study verified, which indicates that exciton dissociation is enhanced. However the absorbed photons at the metal nanoparticles reduce the number of photons which reaches the active layer, thus reducing the cells’ efficiency.

Plain metal nanoparticles without an electron block layer in the front contact act as ohmic links between the blended semiconducting materials in the active layer reducing the cells’ efficiency due to electron – hole recombination on their surfaces.
Intuitively, in conjunction with the above mentioned findings, the following principles for correct design of polymer plasmonic solar cells are presented.

Metal nanoparticles should be isolated from the active material with a very thin layer, such as PEDOT:PSS or encapsulated with a dielectric to allow the effect from a strong local surface plasmon electric field but to prevent recombination of dissociated electron-hole pairs on their surface.

Au nanoparticles are more favorable due to their stronger forward scattering mode compared to absorption[40]. In addition the Fermi level of Au aligns well with PEDOT:PSS 4.7-5.5 eV, which is favourable for the front contact because no extra misalignment of energy levels occurs which could induce charge trapping.

Metal nanoparticles placed in the front contact (before the active layer) should be generally big where the scattering component dominates to minimize losses from absorption of light by the particles. Moreover, calculation of the optimum size for the specified surrounding material to allow efficient waveguide modes (45-65nm for PEDOT:PSS based on the experimental data) and wide space distribution to minimize as much as possible the shadowing effect.

Well encapsulated small metal nanoparticles with a very thin dielectric film should embedded into the active layer. The dielectric will prevent electron-hole recombination on the metal nanoparticle surface, while the strong local plasmonic E-field, will contribute to the improvement of the efficiency of exciton dissociation and consequently the current intensity. Furthermore particles in the active layer must be small in order for the absorption mode to dominate and stronger electric dipole arise from surface Plasmon. The optimum size of nanoparticles should be calculated in

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accordance with the type of the encapsulating dielectric for optimum results. Generally Ag metal nanoparticles have a stronger absorption and local SPR. Although Ag is a good material for particles with strong surface Plasmon and thus enhanced exciton dissociation, the ideal particles for that enhancement should exhibit strong surface plasmon at wavelengths which are out of the useful spectrum for the active layer (Figure 6-12 a). That way all of the AM1.5 G spectrum is utilized by inducing an SPR E-field from photons which are not absorbed in the active layer, in addition the reduction of photons at useful wavelengths which can produce exitons is avoided, since none of those photons are absorbed in the metal particles (Figure 6-12 b). Such particles with SPR in the infrared spectrum are reported to be fabricated with ITO[155].

![Figure 6-12](image)

Figure 6-12 a) AM 1.5G spectrum, P3HT:PCBM spectral response, yellow band for plasmonic structures with enhanced scattering, and blue band for plasmonic structures with strong absorption for enhancing the exciton dissociation due to strong local electric dipole, b) Metallic particles at different positions in the solar cell structure to enhance the efficiency either through the wave guide modes or through the local electric field.

Particles or nanostuctures at the back contact should be a combination of both big and small sizes, carefully designed to achieve the desired effects. In small features generally the absorption mode is dominant, enhancing the surface plasmon wave
which is developed across the boundary of the back contact metal and the semiconducting layer. This could enhance further the exciton dissociation with the strong field. Furthermore, big particles can increase the scattering and redistribution of the unabsorbed photons in the active layer at different angles, increasing the active path and therefore the possibility to be absorbed[114]. Assuming that these features are all part of the back contact, very careful considerations must be taken in the material to be used in order to avoid misalignment of the energy band diagrams–Fermi level which can introduce charge trapping and therefore reduction in the $I_{sc}$ and degradation of $V_{oc}$, since $V_{oc}$ is directly derived from the HOMO-LUMO levels of the donor and acceptor materials.
7 Laser writing of high resolution nanoparticle tracks for sensing applications

Metal nanoparticle thin films (MNFs) between closely separated electrode pads are of great interest for use in gas sensing devices due to their unique physical and chemical properties [3, 18, 186]. Several studies have shown that metal nanoclusters can act as reactive sites to target specific gas molecules [53, 129, 132, 187-189]. Furthermore it has been demonstrated that conduction in dense nanoparticle films is governed by quantum electron tunnelling effects [6, 7, 18, 44, 190]. Thus under the second concept for device applications, laser writing of metal nanoparticles tracks were investigated for fabricating sensing devices.

The ability to have a diversity of laser beam spot sizes simply by using different optics allows the formation of uniform metal nanoparticles films [21, 86, 89, 177] precisely in specified very narrow paths.

In the following sections the fabrication of metal nanoparticle interdigitated patterns on low-cost glass substrates is demonstrated. Furthermore, palladium based nanoparticle sensors made only by laser annealing are tested for the detection of water vapour and hydrogen within controlled environmental chambers. It is shown that the electrical conduction mechanism responsible for the high sensitivity of the devices is related to the inter-particle capacitance and the tunnelling resistance.

For all sensing, elements Corning glass substrates were coated with 15 nm of Pd using a JLS (MPS 500) sputter deposition system. The background pressure in the chamber prior to the deposition was $1.2 \times 10^{-6}$ Torr. Argon (Ar) was used as the
sputtering gas under a pressure of 3.5 mTorr and flow rate of 25 sccm. After metal coating the substrates were mounted on an X-Y translation stage for laser writing.

A number of different approaches were used to focus the laser beam and write different patterns for fabricating working sensing elements. Initially the laser beam was focused with plain focal lens similar to the configuration described previously in Figure 4-2. However the achieved spot resolution was not satisfactory (~0.5mm) for fabricating thin tracks. Sensing elements fabricated with this focal lens configuration had wide paths and no evidence of sensing activity was recorded.

![Figure 7-1](https://example.com/image.png)

*Figure 7-1 a) resolution achieved with plain focal lens and the different patterns b), c) written for sensing elements fabrication.*

To overcome the resolution problem an optical configuration with a reflective objective lens was used to focus down the laser spot as described previously in Figure 4-4.

The samples were mounted on an X-Y translation stage, and the laser beam from an excimer laser was focused down to a circular spot with a diameter of 20 µm. A number of different fluencies and repetition rates were tested to optimize the patterns. The most satisfactory results were obtained for laser fluence of about 1 J cm\(^{-2}\), repetition rate of 20 Hz, and movement speed for the X-Y translation stage of 10 mm min\(^{-1}\). For higher fluences the substrates were damaged substantially and no conductivity was recorded (Figure 7-2 b, c, d). Vice versa for lower fluences the
tracks were partially formed, leaving small bulk metal areas between the formed electrodes which cause short circuits (Figure 7-2 a) left track). Devices with such short circuits did not demonstrate any sensing capability when exposed to gases.

Figure 7-2 SEM in low vacuum to avoid charging, of the laser irradiated paths at different fluence and repetition rates a) left partial track annealed at 0.2J cm⁻² and 20 Hz, right track annealed at 0.6J cm⁻² and 20 Hz b) track annealed at 5J cm⁻² and 15 Hz c) track annealed at 5J cm⁻² and 20 Hz d) track annealed at 10J cm⁻² and 20 Hz. All scale bars are 20μm.

The formation of uniform nanoparticles at such high fluence is slightly different compared to lower fluence. Local irradiation of thin metal films at high enough laser fluence, such as from a focused excimer laser pulse, can induce ablation of the metal [14, 191]. In the presence of a dense background gas the evaporated metal atoms
collide with gas molecules and the ablation plume is strongly confined near the surface of the film. Under these strongly confined conditions, the metal atoms are rapidly thermalized and a significant back deposition of metal atoms onto the substrate occurs as shown schematically in Figure 7-3, allowing nanocluster formation in the area where the laser beam passes.

![Figure 7-3](image)

Figure 7-3 Laser ablation of thin metal film at high fluence forming metal nanoparticles and interdigitated electrodes at a single processing step. Reproduced from [14].

The laser writing process at 1J cm\(^{-2}\) and 20Hz formed two isolated interdigitated metal electrodes on the substrate separated by a path filled with individual metal NPs (Figure 7-4). The interdigitated metallic electrodes have 20 fingers with a 20 µm gap in between (Figure 7-4 a, c). The sensor characterization experiments were carried out on metal nanoparticle sensor devices, which were connected to a measurement circuit using copper wires, as shown in Figure 7-4 a).
Figure 7-4 a) The real sensing device written with laser annealing b) AFM image of the particles formed within the laser irradiated path at 1 J cm$^{-2}$, 20Hz and their size distribution in the inset c) SEM in low vacuum to avoid charging, of the laser irradiated path indicating its dimensions.

To verify the existence of NPs in the fabricated path an Atomic Force Microscope (AFM) from Digital Instruments (Nanoscope IV, Dimention 3100) was used to map the nanostructures between the electrodes (Figure 7-4 b). It can be observed clearly that isolated spherical shaped metallic structures were synthesized during the fabrication process. The NPs are precisely located within the gap and their diameters were in the range from 2 to 12 nm.
7.1 Electrical measurements under different gas exposure

For the humidity sensing experiment the sensors were deployed in the National Physical Laboratory’s environmental testing facilities within a Sanyo 8263 environmental chamber. The temperature during all experiments was maintained at 20 °C. The devices were exposed to water vapour at levels of relative humidity ranging from 40 % to 90 %. A calibrated temperature and humidity meter (Hydrolog sensor Model: NT3-D-CL) was used to monitor the RH. Similarly for the hydrogen sensing experiments a specialized chamber developed in-house was also used to expose the sensors to hydrogen-air mixtures at atmospheric pressure. During this hydrogen exposure test the H₂ concentration was nominally 4 %.

For the electric measurements a computer controlled Keithley 2425 source meter and a Keithley 595 quasi-static, meter were employed to measure and record the changes in resistance and capacitance response signals produced on exposure to the gases.

Although the metal nanoparticles in such kind of MNFs are clearly separated, current flow could be observed. Other studies in similar structures report that the electron transport in such a metal nanoparticle network can be due to tunnelling effects between metal nanoparticles[5]. A voltage across the electrodes, charges the NPs, enabling a rise in the electrostatic field. The Coulomb forces between the charged nanospheres initiates electron transport[46]. At room temperatures the activation energy $E_a$ to initiate a tunnelling event in MNFs is given by Equation 2-22 [47, 48] and
its electrical conductivity by Equation 2-24 [49-51], respectively. From those equations one should expect that the dielectric value of the surrounding medium around the NPs, directly affects the electron tunnelling between the electrodes and the metal nanoparticle array. Thus, by changing the dielectric value of the surrounding medium a substantial change in the flowing current could occur. Thus for a constant value applied potential difference across the electrodes that change in current can be perceived as a modification in the resistance $R$ of the sensor.

The response and the overall resistance of the Pd nanoparticle based sensor which is connected in parallel with a 271 KΩ trimmer resistor is presented in Figure 7-5 as a function of relative humidity (RH). The parallel resistor was used as a compensation mechanism to allow electrical readings at low RH levels, where the actual resistance of the sensor increased to the GΩ range. The relative humidity was varied in six defined steps between 90 % and 40 %. The response and recovery time of the sensor was faster than it takes the humidity (~78 sec) to change in the chamber. The response of a sensing element is given by Equation 3-13, hence for a resistive sensor it is defined as the ratio of the resistance change[123].

$$S_r(\%) = 100 \times \frac{R_0 - R(t)}{R_0}$$

Equation 7-1

where $R_0$ and $R(t)$ is the initial resistance value at 90 % RH and the resistance after exposure at a different RH level, respectively.
Figure 7-5 a) Step response of Pd nanoparticle based sensor for different levels of humidity and b) response of the same sensors over many cycles.

The response of the sensor decreased exponentially with exposure to low levels of RH. This response corresponds well with the exponential nature of conductivity at Equation 2-24 as expected, since water vapour alters the dielectric constant of the air which affects the activation energy $E_a$.

The non-porous materials, glass substrate and metal NPs minimize water molecule retention thereby delivering a rapid recovery time. Moreover the MNFs are suitable structures for interaction with water molecules leading to faster response due to their physical structure. These two factors explain the quick response and recovery time for the sensors observed under investigation. The spikes recorded in the response are not noise but are due to real fluctuations in the RH in the environmental chamber caused by the humidity control system attempting to maintain a fixed RH, which were detectable by the sensor and highlight the usefulness of this device for rapid, sensitive measurements.

The conductivity in a system where electron tunnelling is dominant charge transportation mechanism should increase with temperature according to Equation
2-24. To confirm that tunnelling is the dominant conduction mechanism, rather than contact-limited effects, the resistance of a device was measured as a function of temperature in atmospheric air. A decrease of the resistance with temperature rise was observed. At high temperatures such as 200°C moisture is very low, minimizing the possibility to affect the device resistance. This is suggesting that tunnelling is indeed the dominant mechanism as Figure 7-6 shows.

![Resistance of sensing device as it changes with temperature over time.](image)

Thus, the low power demand due to quantum tunnelling potentially makes this sensor promising for portable metrology applications, although its high resistivity induce difficulties during electrical measurements. An alternative method for electrical measurements in this type of sensing elements could be the recording of capacitance variation.
7.2 Capacitance measurements

In general, the conduction between two nanoparticles can be modeled as a parallel combination of a resistance and a capacitance, an $RC$ equivalent circuit [7, 18]. Hence, the laser nanostructured sensing elements which were fabricated here could be considered as large networks of $RC$ components between the interdigitated electrodes. The capacitance for two parallel plates with area $A$ and separation distance $d$ is given by

$$C = \varepsilon \varepsilon_0 \frac{A}{d}$$  \hspace{1cm}  \text{Equation 7-2}

Therefore, introducing humidity in the structure should change the dielectric constant of the environment and alter the overall capacitance between the electrodes. The typical values of relative permittivity are 1.0006 and 1.0010 for dry air and for saturated wet air[192] respectively. Therefore, the maximum change in capacitance should be 0.0399%.

The recorded capacitance response as a function of RH at 20 °C is presented in Figure 7-7. The response was defined from Equation 7-1 replacing the resistance with capacitance. Initially, the sensor was subjected to 40 % RH and allowed to stabilize. Then the humidity was increased in 10 % RH increments. The time for each step change was kept at 10 min. The response time was again very fast allowing the device to follow the small ripples in RH produced by the humidity control unit. The capacitance at 40 % RH was about $1.52 \times 10^{-11}$ F increasing to $7.45 \times 10^{-9}$ F at 90 % RH, changing in total by two orders of magnitude.
Figure 7-7 Capacitance response of Pd nanoparticle based sensor for different humidity levels.

The sensitivity factor $S_f$ [122] for the laser written devices $S_f = \frac{C_{40\%}}{C_{90\%}} = 490$ is higher compared to other capacitive RH sensors ($S_f = 0.91$)[193]. However, before attributing this high sensitivity to the change in capacitance alone, it is important to consider the nature of the measurement. The Keithley 595 meter is measuring the charge transferred over a time of period into the capacitor on every measurement cycle. The variation of the device leakage current with water vapor based on the resistance measurements indicates that the RH affects directly the resistance of the network. Therefore, the high sensitivity is not due solely to change in $\epsilon*$ responsible for the capacitance variation but to variation of the total effective impedance of the nanoparticles network. It should also be noted that a large network of parallel/series capacitors can be sensitive to small changes in local capacitance amplifying the
overall effect. Essentially, the devices show a large change in the $RC$ time constant on exposure.

### 7.3 Hydrogen sensing

An important factor in sensors is the ability to sense multiple gases with the same device structure, provided that there are no cross interferences. Each gas has a different dielectric constant. Thus, introducing a gas into the surrounding medium will alter the resistance of that sensor due to changes in the electron tunnelling rate between metal NPs. In addition, if the gas reacts with the metal, further modification to the conductivity can occur. Figure 7-8 shows the resistance response of a Pd based sensor when hydrogen was introduced into the chamber. The initial state in the chamber was plain atmospheric conditions which normally contain humid air. Because the humidity level fluctuates over time, a reference conditions had to be established prior to any measurements to hydrogen exposure. To establish a reference condition the chamber was purged with dry air to remove humidity and other possible cross interference gases. The time instant where was the dry air was introduced in the chamber is indicated as zero on the time axis in Figure 7-8. The response decrease indicates the removal of humid molecules from the chamber up to the level where a steady state condition was established.
The response and recovery time were limited to 200 sec and 100 sec respectively. A resistance decrease from $8.06 \times 10^7 \ \Omega$ to $3.47 \times 10^7 \ \Omega$ was recorded, when hydrogen (<4%) was mixed with atmospheric air and introduced into the chamber. The measurements were performed under atmospheric pressure conditions at 25°C. Each time the H$_2$ gas was applied, a gradual saturation in the response occurred decreasing the response time from about 100 sec initially to 35 sec. That gradual saturation is the main reason for the change of gradient at the recoded signal in Figure 7-8. The catalytic function of Pd on H$_2$ allows two processes to occur simultaneously. Pd nanoparticles extract electrons from the hydrogen atoms[194, 195] leading to an increase in the tunnelling current. In addition, H$_2$ molecules react with atmospheric O$_2$ atoms creating molecules of H$_2$O[196], where, they alter the dielectric constant of the environment decreasing further the sensor's resistance.
Furthermore, Pd can react with H₂ producing a coating of palladium-hydride around the NPs. This increases the diameter of NPs and changes their electronic band structure affecting the electron tunnelling rate. The electrical measurements from exposing the Pd nanoparticle based sensor with H₂ shows that the poisoning effect from the reaction of H₂ with Pd is relatively low. The reduction of response time after a few exposures to the gas can be attributed to small residuals from Pd posing which remain on particles surface allowing faster saturation. This double sensing behavior of humidity and hydrogen demonstrates that sensors based on laser nanostructures MNFs can be used for multiple gas sensing, and smart devices made inexpensively over large areas. Furthermore hydrogen is a potential fuel for future portable fuel cells, thus continuously monitoring hydrogen storage facilities with a portable low cost sensor would be of real benefit to any potential build-up of explosive atmospheres.

**7.4 Summary**

It has been shown that it is possible to fabricate nanoparticles in bespoke preprogrammed narrow patterns using only laser writing without the requirement for lithography. This technique was employed to write suitable patterns to fabricate robust nanosensors on low cost substrates.

- Crucial factors for the successful patterning and metal NP formation are: the initial metal thickness, laser fluence, and the low wetability of the substrate by the selected metal.
• Two types of measurements were performed, using capacitance and resistance to record the response of the sensors demonstrating the suitability to measure the sensors response to both methods.

• The localized $RC$ equivalent circuits formed by Pd nanoparticles between the electrodes, significantly improve the capacitance response factor $S_f$ of the sensor when compared to a conventional capacitive sensor.

• The results indicate that the change in the environment dielectric constant with water molecules leads to different current rates affecting the resistance of the device. Additionally, the donated electrons from $H_2$ at Pd particles enhance the current. These results demonstrate the possibility of fabricating low cost multiple gas sensing devices by careful selection of the NP materials and their potential use in portable metrology applications.
8 Metal alloy nanoparticles for enhancing Raman detection sensitivity

Following Equation 2-17 the dielectric constants of the surrounding medium and that of the metal nanoparticles’ are the two main parameters which influence the surface plasmon resonance peak wavelength. In chapter 5 the tuning of Au and Ag nanoparticles SPR wavelength in a controlled manner was demonstrated, by manipulating the dielectric constant of the conductive ITO which served as the surrounding medium, using only laser annealing at various fluencies. However, for applications where a relatively expensive ITO conductive substrate is not required or conductive substrates are prohibited to avoid processes such as quenching of excited photoluminescence and Raman signal in organic molecules for biosensors [56, 197], and gas sensing [178] applications, an alternative method to control the surface plasmon resonance (SPR) is required.

8.1 Tuning the SPR by varying the alloy composition of metal nanoparticles

Mie theory for the extinction of spherical metal nanoparticles (equations 18, 19, 20 chapter 2) implies that the SPR wavelength can be tailored by manipulating the complex dielectric constant of metal nanoparticles. One can expect that mixing two metals during their liquid phase should lead to an alloy in which its dielectric constant value is the superposition of the two metals’ individual dielectric constants provided the metals are miscible. Herein, under the context of laser annealing
metals, the synthesis of metal alloy nanoparticles with tuneable surface plasmon resonances by laser annealing of Ag Au bi-layer films, on low cost glass substrates is demonstrated.

Corning glass substrates were used to deposit metal films in two layers by evaporating silver and gold separately (Figure 8-1). The total film thickness was fixed at 5nm while the thickness of each individual layer was deposited according to formula \((\text{Ag}_x\text{Au}_{5-x})\) where \(x = 0, 1, 2, 3, 4, 5\) in nm.

![Figure 8-1 Au and Ag dual layer initial deposition one different substrate according to \((\text{Ag}_x\text{Au}_{5-x})\) where \(x = 0, 1, 2, 3, 4, 5\) in nm.](image)

The average deposition rate for all materials was 0.1 - 0.2 Å/s. Following the deposition all the samples were mounted on X-Y translation stage moving at a typical speed of 60mm/min where the whole sample could be annealed at the same fluence. A Gaussian profile pulse with 176mJ cm\(^{-2}\) average fluence and repetition frequency of 15Hz was used to nanostructure the films and create uniform coatings of alloy nanoparticles.

After the rapid annealing a strong change in colour was observed in the irradiated paths (Figure 8-2 a-f) compared to the blue-grey initial colour. This colour change is attributed to the generation of metal nanoparticles with SPR absorption in the visible regime. For pure gold the colour of annealed areas is reddish while for pure silver, yellowish. The uniform colour transition from red to yellow across the samples with
different AgAu alloy composition is a strong indication that the dielectric medium of the engineered nanoparticles shifts proportionally with the alloy composition.

![Figure 8-2](image)

Figure 8-2 (a) Ag$_0$Au$_5$ (b) Ag$_1$Au$_4$ (c) Ag$_2$Au$_3$ (d) Ag$_3$Au$_2$ (e) Ag$_4$Au$_1$ (f) Ag$_5$Au$_0$ alloy nanoparticles fabricated using the laser nanoprocessing process and (g-l) their AFM images of different alloy particles.

An Atomic Force Microscope (AFM) was used to morphologically characterize the post-annealed films as shown in Figure 8-2 (g-l). Particles with average sizes in the range 2–50 nm were observed after the annealing process, as shown in Figure 8-3.
Figure 8-3 Size distribution for all different AgAu alloy nanoparticles after laser annealing the initial bilayer metal films at 173mJ.cm⁻¹

For the films of pure Au or Ag, particles with relatively small size distribution 2-20nm were formed compared to alloy particles although all samples were annealed the same time under the same 176mJ cm⁻² fluence. A possible explanation could be that due to single uniform metal layer the irradiation energy is stored and distributed across the film more efficiently, inducing a higher thermal impact which allows the formation of smaller droplets. By contrast in bilayer films, due to the different thermal conductivity (3.17 for Au, 4.29 for Ag in W/(cmK)) and heat of fusion (222.1 for Au, 200.8 for Ag in J/g) [21]values of Ag and Au, some thermal energy is lost at the boundary junction of two metals. This loss of energy resulted in lower delivered thermal energy in the metal bilayer films. Furthermore the fragmentation dynamics
and energy to form alloy particles can be relatively higher [167], thus bigger particles are produced.

Figure 8-4 shows the optical extinction of the annealed MNFs using a spectrophotometer (Varian Cary 5000) indicating the absorption component is dominant in the extinction. Absorptions acquired at random positions gave similar optical characteristics indicating uniformity over the annealed areas.

![Figure 8-4](image)

**Figure 8-4** The optical extinction spectrum obtained from the different alloy composition metal nanoparticle films (i) Ag₅Au₀ (ii) Ag₄Au₁ (iii) Ag₃Au₂ (iv) Ag₂Au₃ (v) AgAu₄ (vi) Ag₅Au₅

Starting from the sample with nanoparticles made from pure Ag the SPR appears at 463nm. As the concentration of Au increases in the alloy the SPR of metal nanoparticle films red shifts and broadens until 556nm where pure Au is the MNFs composition (Figure 8-4 (vi) curve). These observations agree with other studies [87].
The exception to this is for the alloy composition with \( x = 4 \), where the intensity of the peak is higher compared with the pure Ag film. The stronger absorption for that MNF can attribute to the higher density of particles in film (Figure 8-3) where the total absorption in the film can be associated with the superposition of each individual particle’s absorption.

The two peaks which appear in the optical signature of \( \text{Ag}_3\text{Au}_2 \) and \( \text{Ag}_2\text{Au}_3 \) alloy composition MNFs could be attributed to particles with slightly different dielectric constant due to variations in alloy composition or due to particles with different size. To investigate this dual peak phenomenon as well as to verify that the particles are made from an alloy, a theoretical study based on statistical approximation were performed.

For the theoretical model a metal nanoparticle film constituted of individual pure Ag or Au particles in which their size distribution is varying according to the \( \text{Ag}_3\text{Au}_2 \) film real size distribution taken from the AFM data were considered for the simulations. Absorption simulations for each single Ag or Au particle on glass with different diameter (Figure 8-5) were performed using a simulation tool[158]. The theoretical analysis of the size distribution versus absorption peak wavelength revealed a number of key findings. The silver particles have relatively stronger absorption compared to gold with the highest absorption to be induced from the particles with diameter 10nm. The surface plasmon resonance for all different particles sizes of silver is between 430nm to 460nm agreeing well with the experimental data. For gold particles the absorption for all sizes is lower and with a wider full width half maximum. The SPR for gold particles is around 550nm to 600nm. From the statistical
analysis which was performed by combining the Ag₃Au₂ film simulation data at different size distributions (Figure 8-5), comes the observation that increasing the particle size affects the absorption intensity significantly, while the position of SPR absorption peak remains almost unaffected.

![Absorption simulations of a single Ag or Au nanoparticle at range of different size based on the real size distribution of Ag₃Au₂ film.](image)

The Statistical approximate Absorption (SA) of a metal nanoparticle film is the sum of absorptions induced by each individual metal particle, multiplied by the number of events happening in the film, expressed mathematically by the following equation.
\[ SA(\lambda) = \sum_d Q \cdot f(d) \cdot \alpha_d(\lambda) \]  

Equation 8-1

where \( Q \) is the scaling factor based on composition, \( f(d) \) the frequency of events per diameter \( d \), and \( \alpha_d \) the theoretical absorption induced by each metal nanoparticle of that size.

A theoretical study has been performed to determine the SA for the \( \text{Ag}_3\text{Au}_2 \) film (Figure 8-6) composed from a mixture of pure Ag and Au nanoparticles at different diameters and where the distribution of particles diameters were extracted from the AFM data of the real film.

![Graph showing absorption spectra and topography](image)

**Figure 8-6** The statistically approximated absorption for the \( \text{Ag}_3\text{Au}_2 \) film estimated using the real size distribution acquired from AFM characterization which is showing in the inset figure.

The simulation revealed two distinct peaks would be expected to exist for such a film composed of a mixture of Ag and Au particles. Therefore the broad single peak
observed in the real measurements is attributed to alloyed nanoparticles. Furthermore this simulation confirms that the shift in the absorption peak that was observed is due to variations in the dielectric function of nanoparticles, which is caused by the different alloy compositions. Thus the size distribution for $x=2$ and $3$ is not the main reason for the dual maximum in the absorption peaks because those peaks are positioned very close to each other which it cannot explained MNF with two distinct metal particles. These dual absorption peaks should be attributed to small composition variations in the alloy itself. This dual peak absorption phenomenon has significant importance because it demonstrates that energy absorption can be increased over a wide range of wavelengths. This is vital especially for solar cell applications where it is required to increase the absorption efficiency over the entire range of the sun’s radiated wavelengths, even if the primary absorption band of the photoactive material may not be initially able to absorb the energy as a single photon process.

8.2 Alloy metal nanoparticles for enhancing chemical sensor sensitivity

Unlike many other fabrication methods, pulsed laser nanostructuring of thin metal films can be used to easily fabricate alloy metal nanoparticles deployed over large areas at low cost, to fabricate supported nanoparticle surfaces which they can be used directly for sensing applications. To demonstrate the applicability of these engineered surfaces in real sensing applications, properly engineered substrates are used to tune the energy coupling of pump laser with the SPR and investigate how the
position of the surface plasmon resonance affects the optical detection capability of chemical species under this type of resonance surface enhanced Raman signal (RSERS) conditions.

Use of metal alloy nanoparticles can optimize surface enhanced Raman scattering (SERS) by tuning their plasmon resonance absorption close to the laser frequency used to probe the Raman signal from molecules on their surface[146, 198]. However, despite these attractive properties, challenges exist regarding large scale adaptation of plamonic nanoparticle surfaces. Another major challenge in SERS substrates fabrication is the production of uniform MNFs over large area substrates and repeatable tune-ability of their surface plasmon resonances (SPR). The good tune-ability of SPR is required to maximize the energy coupling in SERS which it coincides with the wavelength of the metal nanoparticles SPR and is localized at “hotspot” [144, 146, 199] areas. These “hotspot” areas appear between closely spaced metal nanoparticles where the electric field from the surface plasmons is at maximum due to superposition.
A 1µM aqueous solution of Rhodamine 6G (R6G) was used to investigate the SERS enhancement on the same alloy MNFs which were mentioned in the previous section. A single 5µL droplet was placed on each substrate. All substrates were enclosed in a petri dish for 20 min and allowed to dry, controlling the rate of evaporation of water molecules to ensure uniform distribution of test molecules over the substrates. Distilled water was used to wash off the excess R6G, and the sample was blown dry with nitrogen. Raman spectra were recorded using a Renishaw micro-Raman 2000 system with a 514 nm laser at 4mW and a 25% power attenuator. A (50X) optical lens was used to focus the laser down to an approximately 1µm diameter spot. The detector integration time was set at 1sec and 50 accumulations at the same location were acquired to improve the signal-to-noise ratio.
Figure 8-7 shows the typical R6G Raman scattering spectra taken from the different alloy MNFs with different SPR wavelengths. Different enhancement factors were observed from each different alloy composition. High enhancements in Raman signal were recorded for the films with $x = 2$ and 5. No Raman signal was detected for this concentration of R6G on plain glass substrates (Ref. at Figure 8-7) although high fluorescence recorded.

To determine the relative amplification of plasmonic active substrates compared to plain substrates different concentrations ($1 \mu\text{mol}$, $5 \mu\text{mol}$, $1\text{mmol}$) of R6G on plain glass substrates were applied and measured for various pump laser powers, detector gain and integration time during signal acquisition displayed in Figure 8-8. For each measurement 50 accumulations were used always for improved signal-to-noise ratio. A clear Raman signal from untreated substrates could only be observed for $1\text{mmol}$ solution, a 1000x higher concentration than was deployed on SERS substrates. The plasmonic substrates enhanced the Raman signal of R6G molecules by a 1000 times compared to untreated samples.

![Figure 8-8 Raman signal recorded using plain glass substrates with different combinations of R6G concentration, laser power, integration time and detector's gain.](image)
The method used to apply the test analyte gave uniformly distributed films across the substrates. Therefore, the difference in the enhancement between the different alloy concentration MNFs is considered to be due to different coupling efficiencies in the energy transferred from the surface plasmon resonance to the “hot spots” for the analyzed species. That difference in energy coupling is related to the SPR peak position on MNFs where metal nanoparticles with SPR close to pump wavelengths can couple more strongly with the monochromatic laser light. The intensity of the Raman scattering at the 1361 cm\(^{-1}\) peak versus the SP absorption maximum wavelength is plotted in (Figure 8-9).

One can see that the Raman intensity for the Ag\(_2\)Au\(_3\) with SPR maximum at 514nm is higher than most of the other films. This confirms experimentally that SERS is higher for SPR wavelengths close to the probe laser wavelength. The high Raman intensity for the plain Ag nanoparticles is attributed, we believe, to the strong R6G binding affinity to silver altering the concentration of R6G in that area and hence the Raman intensity known as chemical SERS amplification factor \(\sigma_{\text{SERS}}\) [26, 27, 140]. In addition, the SERS enhancement for pure Ag films is in general stronger than for pure Au hence the enhancement of Ag\(_2\)Au\(_3\) is more significant.
Figure 8-9 Raman intensity versus SPR peak wavelength for all different alloy composition MNFs.

### 8.3 Summary

Summarizing, a method to fabricate large area plasmonic substrates with metal alloy nanoparticles and the ability to engineer precisely their surface plasmon resonance is demonstrated.

- By varying the thickness combination of the initial bi-layer metal films alloy metal nanoparticles can be fabricated with different dielectric constants to tune precisely the SPR according to the alloy concentration.
- The effect of variation in the SPR optical characteristic is attributed to the change in the dielectric function of the alloy nanoparticles from the volumetric contributions of Ag and Au primarily.
• A theoretical study shows that the variation of particles sizes can affect the SPR position but it is insignificant compared to the shift imposed from the change of dielectric constant in alloy nanoparticles.

• Metal nanoparticle films with SPR peak wavelengths close to the excitation pump wavelength can couple more efficient with light inducing higher plasmonic e-fields which enhance the SERS signal more efficiently.

• The tune-ability of the SP wavelength is shown to modify the SERS enhancement of R6G delivered to the nanostructured surfaces.

It is suggested that the laser nanostructuring method could be applied for fabrication of a wide range of metal alloy nanoparticle films over large areas for sensing or energy coupling applications.
9 Conclusions

In this project the suitability of rapid laser annealing technique to fabricate metal nanoparticles with different individual metals or alloys direct within optoelectronic device structures was investigated. The experimental results shown that laser fabrication of metal nanostructures can be used to incorporate particles direct into innovative photovoltaic and gas sensing structures improving their performances.

Metal nanoparticles of Au, Ag, Pd or alloy AuAg were fabricated with a KrF Excimer laser at 248nm on different substrates. Atomic Force Microscopy (AFM) and Scanning Electron Microscopy were used to characterize their size, spatial distribution and the roughness of the nanostructured films. The optical signatures of surface plasmon active metal nanoparticle films were obtained by absorption spectroscopy. It has been observed that capping metal nanoparticles (MNPs) which exhibit surface plasmonic resonance (SPR) in the visible region with a low dielectric constant material such as Al shifts the SPR towards shorter wavelengths. Vice versa encapsulating MNPs using materials with high dielectric constant induces a red shift in the SPR. Excimer laser annealing of relatively sensitive materials such as Indium Tin Oxide induces damages in the material affecting the quality of the film an its physical properties. ITO is a heavily doped semiconductor owing and its low sheet resistance to the oxygen vacancies. Rapid thermal annealing releases oxygen vacancies which result in lower conductivity and number of free carrier densities. The conductivity of Au coated ITO films, which were laser treated, was studied with four probe electrical measurements. It has been observed that different laser fluences induce different resistivity levels. The direct relationship of resistivity in ITO
with the density of free carriers imposes that the dielectric constant of ITO follows the changes according to Drude model. Thus utilizing both the quasi static approximation model to estimate the SPR, and the dielectric constant values calculated, it has been described and verified theoretically that the change of colour (SPR) induced in ITO coated films that were laser annealed at different fluences.

In Chapter 6 metal nanoparticles were fabricated directly onto the solar cell devices. A PEDOT:PSS layer was used as a buffer layer between the ITO and thin metal film to reduce the thermal damage at ITO during the laser nanostructuring process. Adjusting the metal film thickness resulted in metal nanoparticle films (MNFs) with different spatial distribution and size. These plasmonics active substrates were used to fabricate photovoltaic devices. The efficiency and the spectral response of those solar cells were measured with a solar simulator and external quantum efficiency (EQE) set-ups. Measurements obtained from devices with MNFs, which have relatively big particles (65-45nm) and wide separation distances, were shown to have an enhancement in the efficiency. Three factors are associated with this performance improvement; First there is an enhanced charge mobility of PEDOT:PSS film with the incorporation of big metal nanoparticles measured with Hall effect. Second, the dominant forward light scattering component associated with the plasmonic effect of metal nanoparticles surface enhances the light intensity near 650nm as optical measurements with a spectrotrometer and simulations show. Thus an increased number of photons are converted to electrons contributing to the overall efficiency measured with the EQE and current – voltage measurements under a solar simulator irradiation. Third, in dense nanoparticle (NP) films where the localised electric field from SPR is strong, enhanced quenching into the active film
were recorded with photoluminescence. This indicates that carefully design and embedding of nanoparticles which exhibit SPR can enhance the exciton dissociation and consequently the short circuit current.

In Chapter 7 a study of laser writing to fabricate very fine bulk metal with metal nanoparticle hybrid structures was presented. Interdigitated electrode structures with approximately 20μm separation gap incorporated with Pd nanoparticles were fabricated. The structures are characterised electrically to measure capacitance and resistance. In spite of the isolation gap between the electrodes, a current flow of nA was recorded. Current measurements at different temperatures within a dry environment have shown that current flow increases with temperature. An observation which in conjunction with the morphology of the structure infers that current flow is due to electron tunnelling and hopping between particles agreeing well with other studies. The interdigitated structures are used to investigate their capability to sense industrial pollutant gases, humidity and hydrogen. The measurements revealed that the present structures can detect only humidity and hydrogen, showing excellent sensitivity. However the device high resistivity introduces difficulties in measurements. Further research for improvements in signal to noise ratio, lowering the device resistance, multi gas detection capability in addition with portable electronic transducer circuit which has already been built, could all be exploited for commercialization.

The laser annealing fabrication of alloy metal MNFs with different SPR peak wavelengths which can be precisely engineered was presented in Chapter 8. The control of SPR wavelength is due to the change of dielectric function of NP from the
quantitative contribution of Ag and Au metals within the NPs. Adjusting linear the Ag:Au ratio in the initial metal film resulted in SPR changes proportional to the Ag:Au ratio verified by spectroscopic measurements and statistical analysis. All samples with different SPR are coated with a strong photoluminescence material (Rhodamine 6G) and examined for SERS enhancement capability with Raman spectroscopy. The measurements revealed that MNFs with SPRs wavelength close to pump’s light wavelength enhance more strongly the Raman signal, an outcome which agrees well with the theoretical model of resonant SERS.

9.1 Future work – propositions

Metal nanoparticles fabricated using laser annealing on top or within different substrate materials such as a-Si:H, semitransparent a-C:H, Aluminium doped Zinc Oxide and silicon could be used to develop new innovative photonic structures where their optical properties can controlled with the laser annealing power or the doping of the surrounding material (substrate).

Measurements of the actual forward scattering of absorption components per wavelength of the engineered MNFs with an appropriate setup could be beneficial for comparison with the theoretical analysis in Chapter 6.

Use of alloy nanoparticles and periodic arrangement within the solar cells would be interesting to be investigated at a future date. A periodic arrangement of metal nanoparticles could be fabricated with laser interferometric[200] or evaporative lithography[201] or with laser micromachining[202] and anisotropic etch[203].
The fabrication of metal nanoparticles direct into the polymer solar cells devices could be beneficial to link with direct growth of carbon nanotubes (CNTs) on top of the nanoparticles utilising the thermal energy delivered by the laser beam within the same chamber. Such hybrid structure could be used to enhance further the photovoltaic efficiency utilising the superior charge mobility of CNTs to extract and collect the photo-generated charges in conjunction with the enhancement from the plasmonic effects.

Use of different substrates to fabricate gas sensing elements with lower device resistance could be useful for fabricating future sensors with better characteristics.

Finally, it would be useful to integrate appropriate functionalised CNTs with Au:Ag alloy MNFs to capture in the CNTs and amplify the detection signal from diseased cells from human body samples at very low levels with SERS. This technology could create a breakthrough in the early detection of human diseases, allowing early treatment.
10 References


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