Laser ablation of thin carbon nanotube films on glass substrates as transparent field emitters

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Introduction

The excellent field emission properties of carbon nanotubes have been well known for many years.1-3 Recently, transparent nanotube films and transparent field emitters have been studied.4-8 We report transparent field-emitters, produced by spin-coating acid-oxidised multiwall carbon nanotubes (o-MWNT) onto indium tin oxide (ITO)-coated glass slides via an o-MWNT ink. We report substantial changes in the morphology of the o-MWNT layer and an improvement in the FE properties after exposing the films to laser pulses of differing intensity. It is envisaged that this technique could be scaled up as an industrial process for producing truly large area, transparent and cheap FE substrates.

Experimental

Aqueous dispersions of o-MWNT are frequently formed by refluxing nanotubes in a concentrated nitric and sulphuric acid mixture, resulting in the formation of oxygen containing moieties including carboxylic acid groups attached to the nanotube ends and sidewalls. These groups interact with water molecules via hydrogen bonding. Acid treatment also serves to purify nanotubes, removing catalytic particles and amorphous carbon. This method was used to produce an o-MWNT ink with a loading of 3.5 mg/ml. The ink was spin-coated onto carefully cleaned, oxygen plasma treated ITO-coated glass substrates and baked to remove residual water. The sample was exposed to single 25 ns pulses from a 248 nm pulsed UV eximer laser over a range of energies. Each irradiation was repeated at six different sites. The area of the laser spot was 0.134 cm².

Results

SEM images are shown in Figure 1. Figure 1(a) is an as-spun o-MWNT layer on ITO coated glass. This layer is homogeneous across an area of 2.5 x 2.5 cm², except at the very edges. Figures 1(b) - 1(f) show the effects of laser irradiation with fluences 149, 186, 223, 298 and 335 mJ/cm², respectively. In Figure 1(b), cracks can be seen in the ITO layer, due to strong absorption of UV by ITO. The o-MWNT layer appears thinner than the original layer, suggesting that some of the o-MWNTs have been destroyed or removed by the laser pulse. Figure 1(c) and 1(d) show wider cracks in the ITO layer and more damage to the o-MWNT layer. In Figure 1(e) all the o-MWNTs have been entirely removed or destroyed by the laser pulse. The ITO layer has been partially destroyed and ejected from the surface in large chunks, some of which can be seen at the edges of the picture. Figure (f) taken after the highest laser fluence pulse shows that the ITO layer has melted due to the large quantity of energy absorbed.

Fig. 1: SEM images of the substrates after irradiation with fluences 0, 149, 186, 223, 298 and 335 mJ/cm², respectively.
The FE properties were investigated in a diode configuration with a spherical stainless-steel anode. The threshold field ($E_{th}$) was defined as the macroscopic electric field at which 1nA was detected. Figure 2(a) shows $E_{th}$ and the enhancement factor ($\beta$), plotted versus laser fluence. $E_{th}$ ranged from 6.2 V/$\mu$m (at 186 mJ/cm$^2$), to 17.8 V/$\mu$m for untreated o-MWNT. As the laser fluence increases, $E_{th}$ improves and $\beta$ increases. This is due to the o-MWNT laying flat and close together on the untreated substrate, leading to screening and therefore, low $\beta$. As laser fluence increases, some o-MWNT are removed from the substrate and others may be partially lifted from the substrate surface. This reduces screening effects and increases $\beta$. As the laser fluence increases further, $E_{th}$ deteriorates and $\beta$ is reduced. This is due to the removal of o-MWNT from the ITO substrate by the laser irradiation process resulting in FE from fewer sites and on average a much smoother surface. At even higher laser fluences, the incident energy is sufficient to at first partially remove and then melt the ITO layer. FE from the edges of the remaining ITO portions and the metallic islands of the melted ITO layer result in a lower $E_{th}$ and a higher $\beta$ than the original untreated o-MWNT layer.

Transmission (T) spectra (Fig. 2(b)) of the films were measured on a dual-beam spectrophotometer using clean ITO-coated glass as a control. At low laser intensities, T varies slowly as a function of laser fluence. It would be expected that T would increase as o-MWNT are destroyed or removed from the surface. However the surface damage to the ITO layer, visible as cracks in the SEM images leads to scattering and absorption of incident light by the sample and therefore a small reduction in T is observed. At the optimum laser fluence for FE (186 mJ/cm$^2$), T is at 98% that of the untreated o-MWNT layer. At higher laser fluences, T rapidly deteriorates as the ITO surface is modified by the incident laser energy and large surface features increase the amount of scattering from the sample.

**Conclusion**

Flat layers of o-MWNT were spin coated onto ITO-coated glass substrates. This transparent o-MWNT layer was subjected to a single pulse from a UV laser at a range of energies. The resulting substrates were subjected to FE characterisation and $E_{th}$ was measured as 6.2 V/$\mu$m for fluence 186 mJ/cm$^2$. Emission improved with increasing laser fluence, before eventually deteriorating at the highest fluences, as the o-MWNT were removed and the underlying ITO substrate deteriorated. At lower laser fluences the transmission of light through the substrate remained high, whereas at higher laser fluences the transmission was dramatically reduced.

We would like to thank EPSRC (UK) for funding this research via the CBE and Portfolio Partnership programmes.

**References**