Highly transmissive carbon nanotube forests grown at low substrate temperature

By José V. Anguita, David C. Cox, Muhammad Ahmad, Y. Y. Tan, Jeremy Allam and S. Ravi P. Silva*

Corresponding Author(s)*

Dr. J. V. Anguita.
Dr. D. C. Cox.
Mr. M. Ahmad.
Dr. Y. Y. Tan.
Prof. J. Allam

[*] Prof. S. R. P. Silva. Corresponding-Author.

All authors have same address:
Advanced Technology Institute,
University of Surrey,
Guildford. GU2 7XH,
UK.

E-mail: (s.silva@surrey.ac.uk)

Keywords: (Transmissive carbon, subwavelength nanostructures, nanotube forest)

Abstract.

Despite the "darker than black" association attributed to carbon nanotube forests, in this paper we show that it is also possible to grow these structures, over heat-sensitive substrates, featuring highly transmissive characteristics from the UV to infrared wavelengths, for forest heights as high as 20µm. We interpret the optical transmission in terms of light propagation along channels that are self-generated by localised bundling of tubes, acting as waveguides. We show a good correlation between the distribution of diameter sizes of these sub-
wavelength voids and the transmission spectrum of the forests. For the shorter visible and near-UV wavelengths, our model shows that light propagates by channeling along individual vertical voids in the forests, which elucidates the origin for the widely-reported near-zero reflectance values observed in forests. For the longer infrared wavelengths, the mode spreads over many nanotubes and voids, and propagates along a "homogeneous effective medium". We correlate the strong absorption of the forest at the shorter wavelengths in terms of the stronger attenuation inside a waveguide cavity, according to the $\lambda^{-1/2}$ attenuation dependency of standard waveguide theory. The realisation of this material can lead to novel avenues in new optoelectronic device design, where the carbon nanotube forests can be used as highly conducting “scaffolds” for optically active materials, whilst also allowing light to penetrate to significant depths into the structure, in excess of 20µm, enabling optical functionality.

1. Introduction
Carbon nanotubes (CNTs), in particular, multiwalled tubes (MWCNTs) are thermally stable one-dimensional (1D) electrical conductors with transport properties that outperform their nearest rival materials. For example, they exhibit about $10^3$ times better current carrying capacity than copper, twice the thermal conductivity of diamond, 30 times lower field-emission threshold voltage than molybdenum tips, and only half the material density of aluminium, but more than 20 times the tensile strength of steel alloys [1-3]. These properties are additionally improved further if they are normalised per weight, or linear density. Nanotubes are also not compromised by native surface oxide insulating layers, and can be chemically functionalised, even in the plasma phase, in order to optimise their chemical compatibility with a range of organic materials. In particular, the electrical characteristics of MWNCTs make them ideal for enhancing the electrical properties of organic semiconductors using simple mixing techniques [4]. Particular efforts have been invested in optoelectronic
applications such as organic photovoltaics (OPVs) and light emitting devices (OLEDs). [4-7] Other potential optoelectronic applications include optical detectors, [8] indium-tin oxide (ITO) replacement, [9] current injection into other optically active nanostructures, for example Si/SiO₂ and ZnO nanowires, [10, 11] and also devices using electroluminescence properties from nanotubes. [12] However, despite their excellent electrical properties, a possible disadvantage is their strong optical absorption. [13, 14] This could compromise the extent to which nanotubes can be incorporated into optical devices.

Self-assembled nanostructures such as nanotube forests, which consist of dense and vertically aligned MWCNTs that are several micrometers tall, feature record levels of optical absorption, known as “darker than black” materials. Such strong light absorption severely hinders their applicability into optically active devices. This is despite their excellent electrical properties. Their shape make forests ideally suited for carrier transport in regions that are deep inside thick layers of semiconductor materials. So far, reasonable optical transparency in CNT structures has been limited to two-dimensional thin-film layers of percolated random networks of mutiwallled or single walled CNTs, deposited flat onto a substrate from a solution, for example, by spray, dropcast or filtration. [15-17] This technique forms a thin transparent film that is electrically conductive, and has been used successfully as a replacement for the metal-based ITO layer in OPV structures. More recent work shows graphene can potentially be used for this purpose, replacing the CNT film. [15] However, there are still severe engineering limitations, yet to overcome, in the production of large sheets of graphene with sufficiently high quality to minimise electron scattering, and allow for sufficient electrical conductivity to replace ITO in these applications. The optical transparency of 3D carbon structures such as MWCNT forests to date remained poor. [13, 14]
In this paper, we report a method for growing MWCNT forests with high levels of optical transparency at the visible and infrared wavelengths. We show that the transmission mechanism for light transmission is strongly influenced by the formation of vertical voids within the forest that are self-produced during forest growth. These voids span from the top of the forest to the base. We model the light transmission along these voids, and show that these act as efficient light channels, which contribute significantly towards increasing the transmission of light. A similar wave propagation mechanism has been predicted for an anisotropic medium consisting of a flat metal conductor perforated with a disordered array of holes that are smaller than the wavelength of light. [18, 19] In this paper we experimentally determine the optical transmission from our MWCNT forests, and show a close correlation between our results and the theory described for the perforated conductor, in terms of the diameter of the voids observed in the forests. We examine the effect of forest height on optical transmission, and observe a height “window” where optically transmitting forest structures can be obtained.

The possibility of opening these light-channels at the nanoscale, produced by self-assembly, lifts the characteristic “darker than black” attribute to forests, which opens possibilities for such forests being used in optoelectronic devices. In principle, a high-density of these channels will allow light interactions throughout a material that is embedded within the forest. However, the realisation of devices using these structures will require the development of new techniques for producing devices without disturbing the natural assembly of the forest. For example, the addition of organic semiconductors and solvents in the liquid phase. The development of such techniques is outside the scope of the paper, which focuses on the light transmission through forests.
Additionally, we report the growth of MWCNT forests over heat-sensitive substrates. This capability is a key factor for the implementation of CNT technology into current complementary metal oxide semiconductor (CMOS) processes. For example, in the replacement of metals that are currently used for chip interconnect via structures [20-22]. These metals are highly susceptible to electromigration at high current densities (>10^6 A/cm^2), leading to lower reliability as the interconnect dimensions are reduced. The MWCNT forest structures replacing these via structures feature covalently bonded carbon atoms, which mitigate electromigration. Wei et al. [22] showed that the current carrying capacity of CNTs did not degrade even after 350h operating at current densities around 10^{10} A/cm^2. Urgency in material replacement with the continual scaling down of IC components is reflected in the International Technology Roadmap for Semiconductors (ITRS), which states a need for replacement for the year 2015. [23] However, a major obstacle in the integration of MWCNT forests into practical semiconductor devices is their growth temperature, circa 900°C, which far exceeds the limitations before uncontrolled diffusion of dopants in silicon takes place, around 350-400°C. [24] This limitation has resulted in a plethora of CNT-transfer processes. [25, 26] However, complexity and lack of reliable contacts by peel-off processes have deterred commercialisation. Alternative work on low-temperature CNT growth by chemical vapour deposition (CVD) and plasma-enhanced CVD (PECVD) have achieved growth temperatures below the 400°C mark. [27] However, these require the use of ammonia-based gas chemistries, which can reduce the quality of the CNTs, as inferred from the Raman D/G ratios. The literature so far suggests that high quality MWCNT growth (as determined from the D/G Raman ratios) requires growing at high temperature. [28-29]

2. Results and Discussion:
2.1. MWCNT forests growth on low-temperature substrates.

The MWCNT forests were grown on a thin (50nm) transparent membrane of Si$_3$N$_4$ that is supported by a silicon frame, Fig. 1(a). MWCNT forest growth was performed using a photo-thermal chemical vapour deposition (PTCVD) system equipped with wafer back-cooling. [30] In this arrangement, the sample is positioned at the centre of a silicon wafer that is mounted on a flat substrate table maintained at 10°C via a water-cooling circuit, Fig. 1(b, c). This arrangement ensures an effective heat-sink at the back of the wafer. Heat is provided from the top in the form of thermal radiation that is produced from an array of optical lamps, whilst the back of the sample is cooled. Upon exposure to the thermal radiation, the vanishingly small heat capacity of the membrane, compared to the bulk silicon in the die, allows the membrane to reach the high temperatures necessary for the growth of high-quality MWCNT forests, whilst the temperature of the silicon remains low. This effect is exacerbated by the poor thermal conductivity of Si$_3$N$_4$ and poor thermal contact between the membrane and the silicon frame. Modelling using the COMSOL Multiphysics package shows that at thermal equilibrium, the maximum temperature experienced by the silicon frame remains below 300°C, despite the floating membrane reaching peak temperatures close to 1000°C, Fig. 1(b-c). This contrast in temperature is achieved by the continuous cooling applied to the back of the silicon frame. The array of optical lamps is separated from the vacuum chamber by an infrared-transparent window allowing the transfer of thermal radiation to the growth chamber. The details of the growth process can be found in the experimental section.

The selective growth of aligned tubes over the Si$_3$N$_4$ window, shown in Fig. 2(a-d) where the nitride window appears as the square region at the centre of the sample. Raman spectroscopy performed on the forest, using a 514nm wavelength laser excitation source, Fig. 2(c) reveals clear characteristics from high quality multiwall tubes, exhibiting a prominent second-order 2D peak (2700cm$^{-1}$) and a D (1349cm$^{-1}$) to G (1580cm$^{-1}$) peak height ratio of
0.63. [31, 32] Our analysis shows this ratio indicates MWCNT growth at temperatures between 800-1000°C, which is in agreement with our thermal model. The determination of the growth temperature using these Raman peaks is reported in the literature. [29]

The growth rate (measured experimentally) as a function of growth temperature is shown in Fig. 3. The temperature is estimated from ration of the Raman D/G peak intensity ratio, obtained from the forests after growth. This ratio is strongly dependent on the growth temperature, for a given catalyst material, and thus the growth temperature can be estimated. [29] The figure shows that fast growth of MWCNT occurs in a narrow range of temperatures (~700-800°C). The restricted range of growth temperatures suppresses the more highly absorbing regions of the forest during growth (as they become excessively hot), and favours the growth of more optically transparent structures, which remain at the lower temperatures that favour the faster rates of growth. A similar trend in the rate of growth of MWCNTs, reported by Patole et al. [33] attributed the reduction of the growth rate of the nanotubes at excessively higher temperatures to the oxidation of the catalyst.

2.2 Optical properties of the forests.

The remarkable transparency of a CNT forest, despite the density and height of the tubes, around 10⁹ cm⁻² and 20μm respectively, can be appreciated in Fig. 2(b). The transmission spectrum at normal incidence from a number of CNT forests grown to different heights is shown in Fig. 4(a). This shows the 20μm tall forest features high levels of optical transparency, around 80% and 50% in the infrared and visible regions respectively. All forests showed significantly higher transparency in the infrared than in the visible. Fig. 4(b) shows the dependency of the transmittance (on a logarithmic scale) on forest height. The exponential decrease shows consistency with a Beer-Lambert absorption law. The figure shows high levels of transparency for the shorter forests. These become opaque (absorbing) for forest
heights greater than ~70μm for wavelengths in the visible, and ~100μm for the infrared. This case is the onset for MWCNT forest structures with strong levels of absorption such as the “darker than black” forests.

The optical characteristics from the transparent forests contrast with the absorption from other forms of sp² carbon. For example, few-layer graphene (graphite), which exhibits significantly higher absorption, ~ 2.5% per atomic layer, which is also wavelength independent. This difference in the absorption behaviour, despite being the same material, highlights the different way in which light interacts with both materials, which arises from the different geometries of the materials, with respect to the light orientation. This gives rise to non-isotropic optical behaviour. This non-isotropic behaviour is also observed in the transmission spectrum from our forests at different angles of incidence to the normal, Fig. 4(c). This shows that the high level of transparency is maintained upon increasing the angle of incidence by up to 20° to the normal. However, on increasing this further to 45°, the infrared region experiences a significant reduction in the transmission, whilst the visible and UV light do not experience such a strong reduction in the transmission. As a reference, the figure also includes the transmission from non-aligned CNTs, which were grown for the same duration as the 20μm forest. These reveal significantly higher absorption across the entire spectral range.

Our observations are in agreement with those reported by Ni et al. [34] They measured the transmission at two wavelengths from a similar MWCNT forest grown on a quartz crystal, albeit of higher density than in our work. They observed significantly higher absorption at the shorter wavelengths (473nm) than the longer wavelengths (633nm), similarly to our observations. A faster increase in the absorption with angle to the normal, for the longer wavelengths than the shorter wavelengths was also reported. Additionally, they showed strong differences in the absorption between a laser beam incident on the forest with
its electric field oriented co-polarised (along the tube axis) and cross-polarised (perpendicular to the tube axis). They reported significantly higher absorption for the cases where the light was co-polarised with the long axis of the MWCNTs. This was attributed to the mechanism for higher light absorption with increasing angles of incidence to the forest for the case of co-polarised light than cross-polarised light. It also predicts a stronger absorption for the case of light incident on randomly-oriented MWCNTs, Fig. 4(c) than for the case of normal incidence on a MWCNT forest, as in this case, the light is always cross-polarised with the nanotube axis. Zhang et al. [35, 36] showed both light transmission and luminance from filaments made from MWCNT ropes obtained by drawing and winding tubes from a forest, and observed a dependency of these optical properties on the polarisation of the light relative to the orientation of the ropes. The strong dependency of the optical properties of the forest on the orientation relative to the light beam, opens possibilities into optical applications, for example, as wavelength-selective variable optical filters.

Our nanotube forests revealed the presence of localised bundling of the tubes, which gives rise to the formation of vertical channels (voids) within the forest, Fig. 2d. These channels appear as dark columns in the cross-section of the forest, as highlighted in the figure, where the marked line in the centre of the oval marks the width of the channel. The channels run vertically along the height of the forest. The openings of the channels appear at the top surface of the forest as darker areas. Contrast enhancement of the top surface of the forest, Fig. 4(d) inset followed by image analysis on over 4000 channels shows that most of these are narrower than 100nm in diameter, with a rapidly decreasing population of diameters up to around 500nm, Fig. 4(d). The number of channels wider than 500nm is small.

Modelling light transmission through channels of these dimensions using COMSOL Multiphysics, reveals that although the diameter of the channels is smaller than the
wavelength, light can still propagate to significant depths inside the forest, Fig. 5(a-d). In the figure, light propagates from left to right. The figure shows that in the infrared region, Fig. 5(a, c) the wavelength is significantly greater than the diameter of the channels, and the mode extends over several channels and nanotubes that are adjacent to each other, propagating along them simultaneously. In this case, the wave is oblivious to the details in the structure of the forest, and experiences a “homogeneous effective medium” (HEM) as described by Pendry et al. [19] This transmission mechanism takes place for wavelengths that are greater than the features in the forest, up to a cut-off wavelength $\lambda_c = 2a(\varepsilon_h\mu_h)^{1/2} \sim 2a$ for air, where $\varepsilon_h$ and $\mu_h$ are the relative permeability and permittivity of the material filling the voids with diameter $a$. [19] Our statistical analysis of void diameters show these voids appear in significant numbers from diameters up to ~ 500nm, which corresponds to a transition in the optical transmission spectrum around 1000nm. For the case of the shorter wavelengths, the light is able to resolve the individual features of the forest, and the homogeneous effective medium mechanism no longer applies. Instead, the light experiences transmission by “channelling” through the individual channels created within the forest, Fig. 5(b, d). We propose this channelling effect to be the main mechanism for light propagation at visible and ultraviolet frequencies.

Additional evidence for a transmission mechanism based on channelling may be ascertained from the transmittance results in Fig. 4(b). These reveal Beer-Lambert absorption lengths of 20µm and 40µm for illumination at wavelengths of 500nm and 2000nm respectively. These results are in excellent agreement with the attenuation that is expected from a wave travelling along a cylindrical waveguide, which is proportional to $\lambda^{-1/2}$ for wavelengths that are shorter than the cut-off wavelength of the waveguide.
The attenuation of the wave as it travels through the channel can be observed in Fig. 5(b, d) as the wave propagates along the channel from left to right. The attenuation from the wave depicted in Fig. 5(d), obtained from the model, is shown in Fig. 6. This figure depicts the time-averaged power flow of the mode (in a logarithmic scale) as it travels through the channel. The result from the model is in agreement with the Beer-Lambert behaviour that is observed experimentally from our forests in Fig. 4(b).

In terms of the extent of the interaction, the waveguide effect predicts the shorter wavelengths experience significantly stronger absorption than the longer wavelengths, with a \( \lambda^{-1/2} \) dependency. This observation is characteristic from the forests. For the infrared wavelengths, where the mode spills over many channels and tubes, it is possible that the mode still experiences waveguiding effects that cover a wide number of channels and nanotubes. In this case, we expect the mode to cover a region over the forests of similar proportions as its wavelength (several micrometers), which would engulf many channels and nanotubes to propagate the mode, acting as the HEM.

For the case of the shorter wavelengths, the localisation of the wave into a narrow waveguide, as the light enters the forest, gives rise to an enhancement of the electric field strength inside the forest and close to the surface, compared to the wave just prior to entering the forest, Fig. 5(b, d). The model suggests that the stronger field gives rise to stronger interactions with the forest, which lead to stronger absorption at the shorter wavelengths. It is possible that this stronger interaction may lead to the excitation of a \( \pi \)-plasmon along the nanotubes, which causes additional absorption at wavelengths shorter than 200nm. The enhancement of the electric field as the light enters the forest is not observed as pronounced for the infrared case, as the mode is spread over many channels, and the localisation is not as severe.
Our model suggests that for the case of wavelengths that channel along individual voids, (those in the UV-VIS-NIR regions, shorter than ~1µm), the optical mode transmits along individual channels that are composed only of air. The SEM images, Fig. 2(d) show the presence of some small amounts of carbon inside these voids. This is attributed to the presence of some imperfections in the verticality of the tubes in the forest, and also, due to some misalignment at the base of the forest, due to random tube growth at the very early stages of growth, just prior to self-arrangement into vertical forest structures. Apart from these exceptions, the SEM images show that for most of the void structure, the assumption that the voids are composed of air holds mostly true for the majority of the cases. This result indicates that the index of refraction of the forest, \( n_2 \), as experienced by the mode travelling through the air in the voids, will be close to that of air, \( n_1 \). From this, we infer the reflectance \( R \) of the forest at the air/forest interface, given by

\[
R = \left| \frac{n_2 - n_1}{n_2 + n_1} \right|^2
\]  

(1)

will be capable of reaching extremely low values, since \( R \to 0 \) as \( n_2 \to n_1 \). This result, derived from the wave guiding effect shown by the model, is in strong agreement with the widely reported experimental observation of extremely low values of reflectance for MWCNT forest structures. The condition of \( R \to 0 \) is necessary for their behavior as "darker than black" materials. This is inferred from Kirchhoff's law: \( A + R + T = 1 \) where \( R \) is the reflectivity, \( A \) is the absorptivity and \( T \) is the transmittivity. For the case of "darker than black" forests, \( R \to 0 \) and \( T \to 0 \), consequently \( A \to 1 \). For the case of the optically transmitting forests such as those described in this work, \( R \to 0 \) and \( A \to 0 \), consequently \( T \to 1 \). For both types of forests, the condition that \( R \to 0 \) must be met. For the case of transmission at the longer IR
wavelengths, the mode travels through a HEM that is composed mostly of air. This is given by the fact that the tubes in the forest are ~ 20nm in diameter, with an average tube separation ~300nm (on average, taking tube bundling also into account), resulting in large air-filled space separations between the tubes. This separation results in a low average value for the index of refraction for the HEM (albeit always greater than $n_1$), which results in low reflectance values. Despite the very low reflectance values of the forests in both wavelength regimes, our model predicts that in the channeling mode (UV-VIS-NIR), the reflectance can be lower than that at the longer wavelengths (HEM case), since the mode is travelling only through air.

3. Conclusions

Despite the "darker than black" association that is attributed to MWCNT forests, in this paper we have demonstrated that it is also possible to grow these structures with highly transmissive characteristics, ranging from the near UV to infrared wavelengths, for forest heights as high as 20µm. These also feature some degree of optical transmission when taller: 50µm tall forest feature ~20% transmission in the visible, and 70µm tall forest ~20% transmission in the infrared. The realisation of this material can lead to new avenues for engineering new optoelectronic devices. In these, the MWCNT forests, made from highly conducting sp$^2$ carbon, may be used as electrically conductive “scaffolds”, for example, to house an organic semiconductor embedded within the forest. This would enable electrical connectivity between the surface of the substrate and the bulk of the semiconductor, whilst also allowing light to penetrate to significant depths into the structure, in excess of 20µm, which would enable optical activity. We have shown this level of optical conductivity for moderately dense forests of MWCNTs of the order of $10^9$ cm$^{-2}$, which feature tube separation spacings around 300nm.
We have interpreted the optical transmission behavior of the forests in terms of wave guiding effects through holes created in the medium that are sub-wavelength in dimensions. For the case of light at the visible and near-UV wavelengths, our computer model shows that the mode of light is able to penetrate through the forests by channeling along the vertical voids in the forests. Our SEM observations suggest these voids are created as a consequence of localised bundling of adjacent MWCNTs. For the case of wavelengths in the infrared, the mode channels over a spread of many nanotubes and voids. These form a HEM, as has been described in earlier reports. The HEM features a low average density and low index of refraction.

Our description of optical transmission though waveguide opening in the forest is in unison with the widely reported experimental observations of extreme low values of reflectance from forests structures at visible wavelengths ("darker than black" materials). Our interpretation accounts for this, as the light does not experience a change in medium upon entering the forest at the air/forest interface, since it is waveguided along air-filled voids. For the case of transmission at infrared wavelengths, the low value for the index of refraction of the HEM also accounts for the low reflectance, albeit we suggest the reflectance in this wavelength regime to be greater than in the "channeling" UV-VIS-NIR regime. We have described the stronger absorption of the forest at the shorter wavelengths in terms of the stronger attenuation that a wave experiences inside a waveguide at the shorter wavelengths, according to the $\lambda^{-1/2}$ attenuation dependency of standard waveguide theory. It is noted that the 'highly transmissive' regime is dependent on the carbon nanotube alignment and packing density of nucleation sites. The best transmission is obtained when there are no carbon nanotubes. This sets a limit on the maximum nanotube density.
We have shown the capability to produce these optically-transparent MWCNT forests structures by means of using a system that provides thermal energy for forest growth via optical heating, whilst providing thermal cooling at the back of the sample. We have shown that such a system can be operated in a regime that favours the growth of transparent MWCNT structures. In these, excessive localised heating of the light-absorbing regions of the forest experience a strong reduction in their growth rates, and therefore become suppressed. This has previously been attributed to excessive oxidation of the catalyst. The growth of transparent structures in the forests feature optimum heating, and therefore become prominent features in the forests.

We have used a floating-membrane technique combined with top-down optical heating and a heat sink below the substrate to maintain a low substrate temperature during the growth of our MWCNT forests. Our thermal model shows that this thermal arrangement allows the membrane to reach the high-temperatures necessary for the growth of high-quality MWCNT structures (circa 800°C), whilst the bulk of the substrate remains at lower temperatures, compatible with CMOS processing (below 300°C). This thermal arrangement allows for this compatibility without the requirement of ammonia gas chemistries during MWCNT growth. Raman measurements performed after MWCNT growth are in agreement with results from the thermal modeling. Using ammonia gas chemistries to further reduce the growth temperature could result in additional reductions to the maximum temperature that the substrate is subjected to during processing. We suggest this floating-membrane technique could be implemented into current IC production facilities, where multitudes of such membrane structures could be defined over silicon wafers, to define the areas for the growth of MWCNT forest. These highly-conductive and electromigration-resilient forest structures could be used for applications such as interconnecting via-structures. The additional
properties of optical transparency allow extending the applicability of the forest to optoelectronic applications, for example, in flat panel displays or for electrical connectivity in photovoltaic applications.

4. Experimental

Substrates with a 50nm thick Si$_3$N$_4$ floating membrane in a silicon frame were obtained from Agar Scientific Ltd. Fe catalyst layers were sputter-deposited using a sputter coater system from JLS, using a pure Fe target and Ar gas (25sccm) at a pressure of 5mTorr, using a dc power supply at 430V and 0.2A, and a separation of 65mm. MWCNT growth was performed using a Surrey NanoSystems 1000N system, using hydrogen (100sccm) and acetylene (5sccm) at a combined pressure of 2 Torr. Eight halogen lamps, rated at 1kW in total and housed in a gold-coated reflector, illuminated the wafer at a distance of 15cm. The power used for the growth was 200W. The back of the silicon carrier wafer was water-cooled to 10°C using a water chiller. A more detailed account of the equipment used can be found in [30]. The growth process consisted of an annealing step in hydrogen at the set optical power for 5 minutes, followed by the introduction of the acetylene gas. MWCNT forests of different heights were obtained by adjusting the time that the samples were exposed to the acetylene. The heating and cooling times are fast, due to the rapid optical heating and continuous water cooling. Non-aligned MWCNTs were grown on the membrane by avoiding the annealing step. Electron microscopy was performed using a Quanta 200 environmental scanning electron microscope (ESEM) from FEI. Raman spectroscopy was performed using the 514nm line from an argon ion laser for excitation. Raman measurements were obtained at the centre of the MWCNT forests. Optical UV-VIS-NIR spectroscopy was obtained using a Cary 5000
system from Varian. The nanotube density was estimated by SEM imaging, by counting the number of CNTs growing over an area on the substrate.

Acknowledgements

We gratefully acknowledge the technical support from Surrey NanoSystems Ltd

References


[23] International Technology Roadmap for Semiconductors (http://www.itrs.net/)


[34] C. Ni, P. R. Bandaru, Carbon, 2009, 47, 2898.


Figure 1. (a): Schematic of the PTCVD system used for growing transparent MWCNT forests, and placement of sample in the chamber. Inset: schematic of sample geometry showing the membrane on top. (b) Thermal model of the sample mounted on the silicon carrier wafer at thermal equilibrium. (c) Close-up view of sample showing the hotter membrane compared to the bulk of the silicon in the sample.
Figure 2. (a) Selective growth of a MWCNT forest over the membrane, bar: 100μm. (b) Image of the 20μm tall forest sample under normal desktop illumination, showing significant transparency in the visible. (c) Raman spectroscopy from the forest obtained using an excitation laser source of 514nm wavelength. (d) Cross-section of forest showing vertical alignment and the formation of channel voids, highlighted in green. Bar: 10μm.
Figure 3. Growth rate of the MWCNT forest as a function of temperature by optical heating, deduced after growth by Raman spectroscopy for two Fe catalyst film thicknesses.
Figure 4. (a) Optical transmission from forests of different heights. The absorption from the annealed catalyst film is shown as the dashed line. (b) Transmission vs forest height in the visible and infrared wavelengths in a semi-logarithmic scale. (c) Transmission through the 20μm tall forest for different angles of incidence. The transmission from non-aligned MWCNTs (inset) is shown for comparison, bar: 5μm. (d) Histogram showing the distribution of channel width sizes, measured from the contrast enhanced SEM image of the top surface of the forest, inset. Bar: 50μm.
Figure 5. Electric field of waves travelling from left to right, transmitting through a 20μm (a, b) and 40μm (c, d) tall forest, for wavelengths of 2000nm (a, c) and 5000nm (b, d). The forest features a 500nm void. Figures (c) and (d), (depicting the longer forest) have been compressed laterally, for sake of clarity.
Figure 6. Time-averaged power flow of wave travelling trough void shown in Figure 5(d) as a function of distance travelled through forest, obtained from the model.
The table of contents entry

Although carbon nanotube forests are synonymous with optical opaqueness, we show the growth of up to 20μm tall forests, featuring optical transparency in the visible and infrared. Additionally, they are grown on heat-sensitive substrates below 300°C, opening prospects for carbon optoelectronics. We show transparency occurs in the visible by light channelling through subwavelength voids in the forests, acting as waveguides.

Keyword: (Transmissive, subwavelength nanostructures, nanotube forest)

By José V. Anguita, David C. Cox, Muhammad Ahmad, Y. Y. Tan, Jeremy Allam and S. Ravi P. Silva*

Corresponding Author*

Title: Highly transmissive carbon nanotube forests grown at low substrate temperature

Supporting Information should be included here

There is no supporting information for this manuscript