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## Carbon nanotube net as a conductive and transparent film for solar energy conversion

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**Abstract:** Vertically aligned silicon nanowires arrays have been grown through a metal-assisted chemical etching method, giving a heavily absorbing surface. Over this surface, a transparent and conductive net of carbon nanotubes has been formed by chemical vapour deposition. The optical characterisation of the net has been performed by the study of its hemispherical reflectance, and the electrical properties have been obtained by four-point probe method. A high transmittance of the net (over 99%) in the 300–900 nm range is reported. Also, a good sheet resistance value has been obtained (around 3 k $\Omega/\square$ ) for such a thin carbon nanotube net.

**Keywords:** nanotechnology; silicon nanowires; carbon nanotubes; conductive; transparent.

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Carmen Morant received her BSc (Physics) in 1986, MSc (Applied Physics) in 1987 and PhD (Applied Physics) in 1990, all of them in the Universidad Autónoma de Madrid, Spain. From 1991 to 1993, she conducted her scientific postdoctoral research in Lawrence Berkeley Laboratory, California (USA). Currently, she is a Professor of the Department of Applied Physics at the Universidad Autónoma de Madrid (Spain) and she also worked six months as Visiting Professor at the Trinity College of Dublin. She is author of 63 scientific publications, four patents and participation in 23 Research Proposals, leading four of them. The research topics currently being developed focus on the synthesis and characterisation of carbon nanotubes, nanowires and other nanostructured materials for energy storage and development of electrodes in lithium-ion batteries.

Eduardo Elizalde received his BS in 1975 from Universidad Complutense de Madrid and PhD in 1984 from Universidad Autónoma de Madrid, Spain. From 1985 to 1990, he conducted his scientific research in Laboratoire de Physique des Solides at Université Pierre et Marie Curie (Paris, France), Surface Science Department at the National Institute of Standards and Technology (Gaithersburg, USA) and Applied Physics Department at Universidad Autónoma (Madrid, Spain). Author of over 80 scientific publications in various international journals, has been responsible for more than 20 scientific research projects and holds five patents. His current research includes design and fabrication of new-generation energy storage devices such as solar cells and lithium-ion batteries based on silicon nanowires.

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## 1 Introduction

In the last few years, silicon nanowires (SiNWs) have attracted a lot of attention for their low reflectance [1], quantum confinement properties [2] and new p-n junction possibilities [3]. These properties made them a very promising technology for solar energy conversion [4], nanoelectronics [5], energy storage [6] and many other fields. In spite of this, SiNWs present several drawbacks that are still to be solved. Among those disadvantages we can note their relatively high surface recombination [7] and the fact that their abrupt morphology does not allow a proper contact with common conductive materials [8]. For this reason, it becomes necessary to find an effective method to perform an electrical contact all over the surface without degrading the good optical properties of the SiNWs. This is the focus of the work, we report the growth of a highly conducting and transparent carbon nanotube (CNT) net which connects every nanowire of the surface through an easy, cheap and scalable method. The use of the CNTs as a conductive and transparent film has obtained popularity recently. The most used synthesis methods are the floating catalyst method [9–11] and the deposition method [12,13]. The first one has proved to be a very adaptive and simple method but lacks obtaining high transmittances. The last method is very controllable but is commonly very laborious and the contact with the underlayer material is not as good as in other methods. The method presented in this work shows a very good conductive properties with a very high transmittance (over the 99%) while keeping a good contact with the underlayer material.

## 2 Experimental

The SiNWs were synthesised through a metal-assisted chemical etching (MACE) [14,15] on p-type (100) monocrystalline (1–10  $\Omega$  cm, boron-doped, 300  $\mu$ m) silicon wafers.

The growth of CNTs was carried out using a SiNWs-covered surface as substrate. The synthesis of CNTs was performed as described in a previous paper [16] and only a short description is included here for reference. First the Mo and Co catalyst was deposited by a dip-coating technique into Mo and Co acetate solutions followed by a calcination. After that, the CNTs synthesis was made using a thermal CVD system at atmospheric pressure. The samples were heated at 800°C under an argon and hydrogen flow, then the gas mixture was replaced by a nitrogen mixed with ethanol flow.

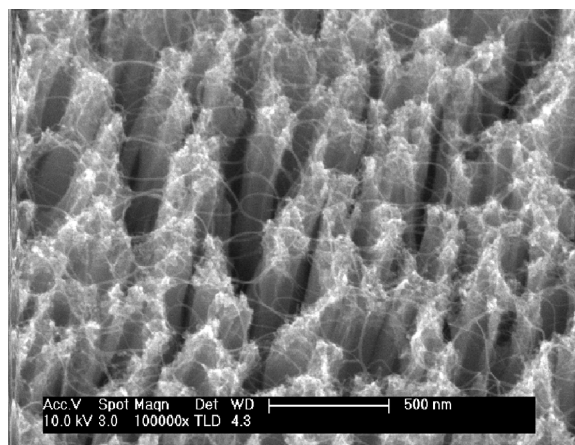
The surface morphology and the cross section of the samples were analysed by using scanning electron microscopy (Philips XL30 S-FEG). A spectrophotometer (Lambda 900) in the wavelength range between 250 nm to 900 nm was used to obtain the optical properties of the surface. The electrical characterisation of the surface was systematically performed by the use of a four-point probe system (Dumas four-point probe head with a Keithley 619 Electrometer/Multimeter and a Keithley 220 Current source).

## 3 Results and discussion

The method used for the synthesis of the CNTs produces vertically-aligned single-walled carbon nanotubes [16] when planar silicon or quartz substrates are used. However,

it was found by SEM images that in our case it leads to a net formation as can be seen in Figure 1.

**Figure 1** Carbon nanotubes growth over silicon nanowires



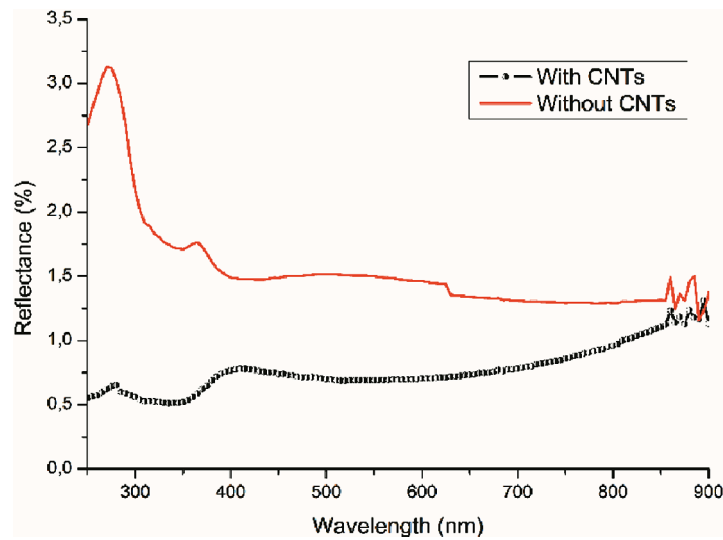
This net formation may come from the fact that the nucleation points of the catalyst are in the side-walls and peaks of the SiNWs. These surfaces are rather parallel to each other, so when the CNTs grow perpendicular to them, they find a neighbouring wall or peak to which they get attached, interconnecting all the SiNWs. It was also found that as it get closer to the base of the SiNWs, the amount of nanotubes is lower. The authors believe that the narrow space does not allow the Mo and Co acetate solutions to penetrate and nucleate. Because of that, all the CNTs are found in a very low depth close to the surface. Through SEM images analysis and confocal Raman depth profiles (not shown), the average thickness of the net was estimated to be around 200 nm.

The optical properties of the CNTs were obtained by the analysis of hemispherical reflectance measurements. This technique was selected because the high absorption of the SiNWs would not allow the use of other techniques as absorption configurations or ellipsometry. Two sets of samples were fabricated to isolate the contribution from the CNT net. The first set was composed of SiNWs samples with CNT net over them. The second one, SiNWs samples with all the CNT growth procedure but without introducing alcohol in the CVD during the thermal treatment, so the CNTs did not grow. By this way we could distinguish the properties of the CNT net removing parameters associated with catalyst presence or reactions with hydrogen. The results obtained are displayed in Figure 2, where it can be seen that the reflectance of the sample with SiNWs is very low, decreasing even further with CNTs.

From these results it can be obtained the absorption of the CNT net by subtracting the measurement of the SiNWs to the one of the SiNWs with CNTs. Performing the mentioned calculation, the average absorption of the CNT net, on the wavelength range from 250 nm to 900 nm, is 0.8%. This means that the transparency of the CNT net is 99.2%, which is very high in comparison with other results from the literature [9–13] with other CNTs layers.

The electrical properties of the surface were measured by a four-point probe system. The measurements were performed over samples in different stages of the CNT net grow and with different treatments. In Table 1, we summarised the results, where the reference Si corresponds to silicon substrates before the growth of the SiNWs and CNTs. The reference Si + SiNWs correspond to the same substrates as before but with SiNWs grown on them. The reference Si + SiNWs + CNTs correspond to samples after the growth of the SiNWs and CNTs. The reference Si + SiNWs + OXIDATION correspond to samples heavily oxidised by a wet oxidation on a CVD system after the growth of the SiNWs. Finally, the samples Si + SiNWs + OXIDATION + CNTs were the oxidised samples but with CNTs on them.

**Figure 2** Hemispherical reflectance measurements on treated silicon nanowires without carbon nanotubes (red line) and silicon nanowires with carbon nanotubes (dot line) (see online version for colours)



**Table 1** Sheet resistance values of samples in each step of the CNT net growth process

<i>Samples</i>	<i>Average sheet resistance (<math>\Omega/\square</math>)</i>	<i>Standard deviation (<math>\Omega/\square</math>)</i>
Si	70	$\pm 5$
Si + SiNWs	80	$\pm 5$
Si + SiNWs + CNTs	3000	$\pm 500$
Si + SiNWs + OXIDATION	$\infty$	
Si + SiNWs + OXIDATION + CNTs	3200	$\pm 500$

We found that the samples with carbon nanotubes show the same sheet resistance ( $R_s$ ), regardless of the substrate on which they were grown. This can be easily seen in Table 1, as samples Si + SiNWs + CNTs and Si + SiNWs + OXIDATION + CNTs have almost the same  $R_s$  value despite of their substrates had different resistance value. The mentioned fact is even clearer in the case of the oxidised samples Si + SiNWs + OXIDATION and Si + SiNWs + OXIDATION + CNTs. Before the CNT growth, the  $R_s$  of the oxidised sample was so high that it was impossible to measure, after the CNT

growth process it changed its  $R_s$  value to  $3.2 \text{ k}\Omega/\square$ , a value in the range of the other samples with CNTs (around  $3 \text{ k}\Omega/\square$  for the samples directly growth over the bare SiNWs). This proves unequivocally that the measured  $R_s$  was the one of the CNT net without any interaction from the substrate. The average sheet resistance, obtained from all samples with carbon nanotubes, was  $3 \text{ k}\Omega/\square$ , a very low value for a so thin (nanometric size) and transparent layer (99.2%). The value obtained is in the range of those reported by other groups in the literature with CNT synthesised and deposited by different methods and over different substrates [9–13]. However, in the present work, the low absorbance for the obtained  $R_s$  leads to a better relationship between transparency and  $R_s$ .

The difficulty in the precise control of the CNT net density through the synthesis parameters, is the highest drawback of this method. Opposite to this drawback, this method offers an effective way of creating a low resistance and high transparent interconnected CNT net all over the surface. In spite of the fact that the obtained sheet resistance of the carbon nanotube net is still a bit higher than with other conductive coatings like indium tin oxide, the low affectation of the antireflective properties, as well as the low cost and simplicity of the production process, makes this CNT net formation on SiNWs a very promising choice. Moreover, while the sharp shape of the SiNWs is a huge problem for the deposition of the TCO layers, the CNT net gets benefit from it, being a choice to consider in this developing SiNWs technology.

#### 4 Conclusions

Carbon nanotubes have been grown forming an interconnected and continuous net over the SiNWs by a simple, cheap and easy scalable method. The CNT net has proved to be a good transparent conductive surface, with a transparency of 99.2% and a sheet resistance value around  $3 \text{ k}\Omega/\square$ . The sheet resistance value has been shown to be independent of the kind of substrate used, having even tested isolating ones.

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