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Solution-deposited carbon nanotube layers for flexible display applications

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Abstract

We have investigated two possible fields of application for carbon nanotube (CNT) networks in flexible displays. Transparent and conductive layers of CNTs were spray coated onto glass and plastic substrates. The spectral transmission of the produced layers is almost even for all wavelengths in the visible regime. A sheet resistance of $400\,\Omega/\square$ at a transmittance of 80% was achieved.

Thin-film transistors (TFT) were created on silicon wafers and glass substrates using low-density CNT networks as a semiconducting layer. The process used for device fabrication on glass substrates is fully compatible to application on plastic foils. The transistors reach on/off ratios of more than five orders of magnitude and show device charge carrier mobilities in the order of $1\,\mathrm{cm}^2/\mathrm{Vs}$. These values promise an application in active matrix liquid crystal displays (AMLCD). Issues that need to be addressed are the homogeneity and reproducibility of the device properties.

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1. Introduction

The development of flexible displays is a major challenge for researchers and the display industry. Most materials and processes commonly used for today's flat panel displays cannot be transferred to flexible substrates. Materials like indium tin oxide (ITO), used for transparent and conductive layers, as well as amorphous or polycrystalline silicon, used as semiconductor in thin-film transistors (TFTs), are brittle and therefore cannot be bended. The same holds for the well-established gate dielectrics SiO_2 and Si_3N_4. Another drawback is the processing temperature of 280 °C and above, needed for the PECVD of these layers. Table 1 shows glass transition temperatures for plastic substrates used in this work that are suitable for display applications.

The unique properties of carbon nanotubes (CNTs) promise solutions for some of the mentioned issues. It has been shown that nanotube layers can act as transparent conductors in flexible applications where they are much more robust than ITO [1].

Since nanotubes can also be semiconducting, they have successfully been used to build transistors. Organic semiconductors like pentacene are also well suited for flexible applications and show good electrical performance [2]. Their major drawbacks however are low-charge carrier mobilities in the order of $1\,\mathrm{cm}^2/\mathrm{Vs}$ or less and degradation in ambient air [3].

We have investigated the use of single and double-walled carbon nanotubes (SWNT/DWNT) as conducting and transparent layers, replacing the brittle ITO on flexible substrates and of SWNTs as the semiconducting layer in thin-film transistors. There is no need for alignment since a CNT-network is used instead of single CNTs.

Our approach uses deposition from surfactant solution, which takes place at 80 °C or room temperature in the case

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Table 1
Glass transition temperatures T_g of tested plastic substrates that can be used for display applications

Material	PEN	PES	PAR
T_g (°C)	130	220	180

of CNT-TFT production. It will replace time-consuming and costly vacuum processes and can be scaled to large area flexible substrates.

There have been publications about highly bendable CNT network TFTs using polymers as dielectric layers [4,5]. These polymers have poor electrical performance compared to nonflexible dielectrics like SiO_2 [6]. We use an Al gate with a pinhole free Al_2O_3 formed on top of it by anodic oxidation [6]. The thickness of the Al_2O_3 layer is about 50 nm and it has a dielectric constant of $\varepsilon_r = 9$. The process is compatible with flexible substrates and is used successfully at our laboratory for the production of pentacene TFTs on plastic foils [7]. CNT-TFTs on flexible plastic substrates will be realized in the near future using the described methods.

2. Device fabrication

A variety of nanotube materials were employed. Purified single wall and double wall HiPCo [8] CNTs from Carbon Nanotechnologies Inc. were used to create transparent, conductive coatings. As-prepared (AP-grade) arc discharge SWNTs were used as a semiconducting layer in thin-film transistors.

The CNT powders are dispersed in surfactant solution containing 1 wt% of sodium dodecyl sulfate (SDS) or similar surfactant. The starting concentrations were between 0.05 and 0.2 wt% of nanotube material. After mixing, the suspensions are sonicated using a 24 kHz tip sonicator and a 39 kHz bath sonicator followed by centrifugation at 40 000*g* for 1 h.

2.1. Transparent and conductive layers

Transparent, conductive layers of nanotubes were fabricated by spray coating the suspension onto $50 \times 50\,\text{mm}^2$ glass and plastic substrates of polyethylennaphthalate, polyethersulfone and polyarylate (PEN, PES, PAR) using a conventional airbrush. Since adhesion of nanotubes to glass is very poor, the substrates are coated with a polyimide or a self assembled monolayer (SAM) of 3-aminopropyltriethoxysilane (APTS) prior to CNT deposition. To avoid droplet formation the substrates are heated to around 80 °C during the deposition.

To increase the robustness of the nanotube layers a polyimide which is commonly used as an orientation layer in liquid crystal displays (Sunever SE-130 from Nissan Chemical) is spin coated onto the nanotube network.

The nanotube layers were characterized using four-point probe and spectral transmission measurements. Scanning electron microscope (SEM) and scanning probe microscope (SPM) images were taken of the surface to establish a closer look at the layer structure.

The optical transmission and the sheet resistance were measured on five different points over the whole substrate area. The adhesion of the nanotube layers to the substrate was tested with the scotch tape method.

2.2. CNT thin-film transistors

CNT thin-film transistors were made on doped silicon wafers and glass substrates. The silicon wafers are used as a common gate with a thermal silicon oxide as the gate dielectric. On glass substrates a patterned aluminum gate is created by sputtering and standard lithography. A gate dielectric of aluminum oxide with a thickness of 50 nm is formed on top of the gate pattern by anodic oxidation [6]. After applying a SAM of APTS, the nanotubes are spin coated onto the substrates from solution. A simultaneously applied stream of methanol releases the nanotubes from the surrounding surfactant micelle, so that they can adhere to the silane terminated SAM [9]. After removing the residual surfactant by rinsing in water, the source and drain contacts are formed on top of the nanotube network by standard lithography and liftoff. We are using sputtered titanium or e-beam evaporated palladium. The width (*W*) and length (*L*) of the TFT channels are varied from 50 to 200 μm and 5 to 100 μm, respectively. Fig. 1 shows the schematic configuration and a picture of an actual device.

To minimize leakage currents, the CNT network is confined to the active region by protecting the channel area with patterned photo resist and cleaning the substrate with a CO_2 snow jet [10]. After removal of the protection layer in acetone, the devices are ready for characterization. We use a Keithley 4200 semiconductor characterization system for TFT measurements. Device charge carrier mobilities

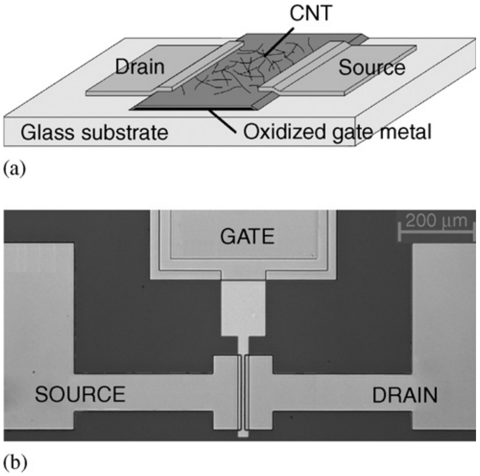

Fig. 1. (a) Concept of the carbon nanotube network TFT on glass and (b) microscope image of a TFT with $W = 200\,\mu\text{m}$ and $L = 10\,\mu\text{m}$.

are calculated using Eq. (1), where d is the thickness of the gate oxide.

$$\mu = \frac{L \cdot d}{W \varepsilon_0 \varepsilon_r} \frac{\mathrm{d}I_{sd}}{\mathrm{d}V_g}. \quad (1)$$

This equation does not take into account that the current flows only through isolated nanotubes. The actual mobility in an individual nanotube itself is therefore much higher than the calculated device mobility.

3. Results and discussion

3.1. Transparent and conductive coatings

After spray coating the nanotube layers and rinsing off the surfactant, the adhesion of the nanotube layer to the substrate is not sufficient. It can be improved by deposition of a polyimide. Fig. 2 shows an SEM image of a spray coated nanotube layer after application of the polyimide top coating. A network consisting mostly of CNT bundles with open and filled interspaces is clearly visible. This shows that the polyimide is not sitting on top of the network, but soaks into the interspaces. Since the polyimide improves the adhesion to the substrate it seems evident that it percolates through the whole layer and gets in contact with the substrate. The sheet resistance increases only slightly (~10%) by the use of the polyimide and it is not clear if this really comes from a higher resistance in the material or if the contact resistance to the four point probe has increased. SPM measurements of a $10 \times 10\,\mu\mathrm{m}^2$ area give an arithmetic mean deviation of $S_a = 12.5\,\mathrm{nm}$, but a ten point height of $S_z = 155\,\mathrm{nm}$ mainly coming from thicker bundles. To minimize the roughness of the layer, the nanotubes need to be very well dispersed and particles and thicker bundles need to be removed from the suspension by centrifugation.

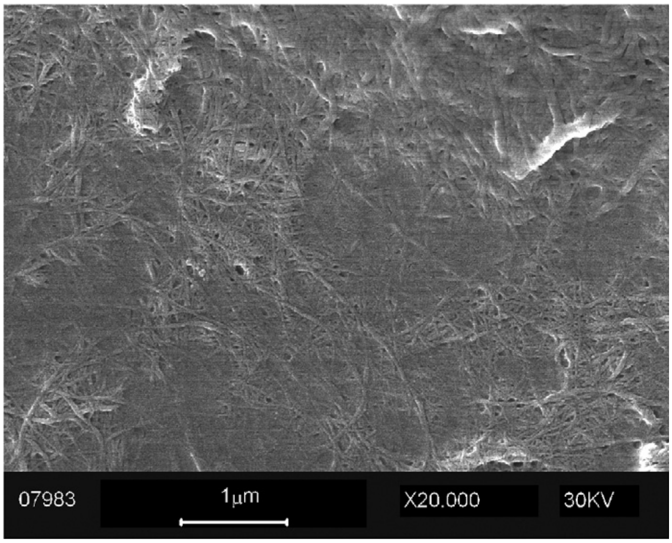

Fig. 2. SEM image of a spray-coated carbon nanotube network with polyimide top coating.

CNT layers with similar thicknesses have diverse values of sheet resistance on different materials. AFM measurements revealed that this is mainly due to different values of surface roughness of the used materials. Our explanation is that a higher roughness leads to a less interconnected network. Best values were achieved on glass substrates with the above-mentioned treatment and on PES foils.

The data of transmission scans for layers of different thicknesses is plotted in Fig. 3. The transmission in the whole visible regime is relatively even. In terms of optical performance the nanotube layers are therefore very well suited for display applications.

A plot of transmittance vs. sheet resistance of ITO on glass and foil as well as CNT layers on glass can be seen in Fig. 4. Obviously the ITO layers have a much higher

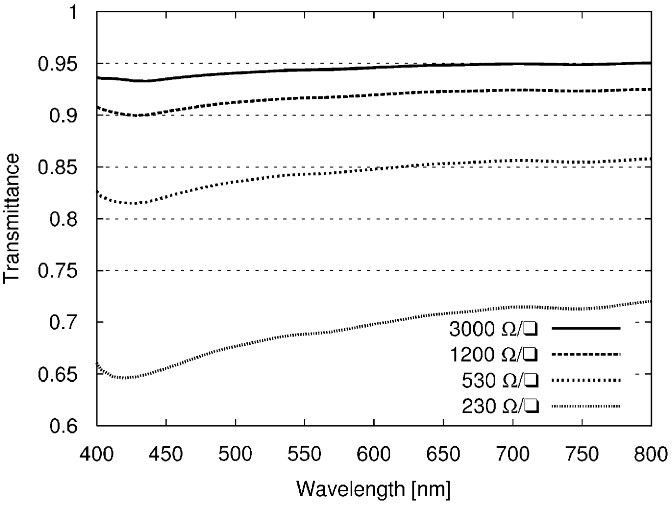

Fig. 3. Transmittance of spray-coated layers with different thicknesses in the visible regime.

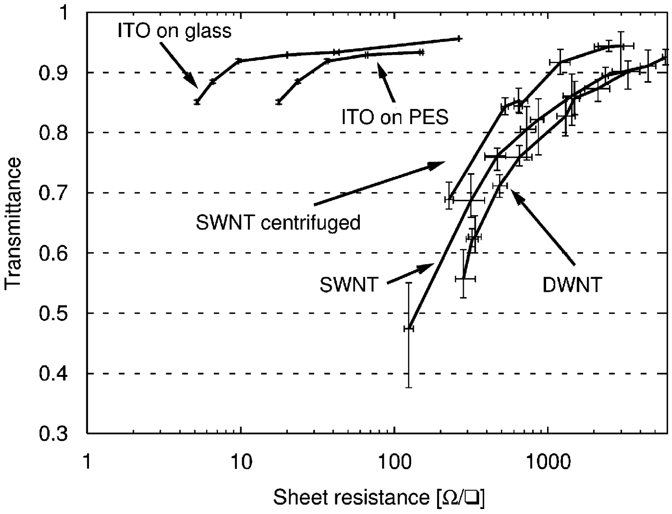

Fig. 4. Transmittance in the visible regime vs. sheet resistance for sputtered ITO layers after tempering and spray coated CNT layers on glass without polyimide top coating; error bars show the range of values for five measurements over the whole substrate area.

performance than the CNT layers. On plastic substrates the ITO sheet resistance is higher than on glass. The foils also bend with increasing thickness of the deposited ITO and it has been shown that the resistance rises very quickly when such substrates are being bended or stretched [1]. This is not the case for nanotube layers.

With identical processing parameters SWNT layers show a lower sheet resistance than DWNT layers, making them better suited for conductive layers. After cleaning the suspension from particles and bigger nanotube bundles by centrifugation, the transmittance can be increased significantly. By producing a highly dispersed suspension with single nanotubes and minimal impurities, it might be possible to improve the performance even more. The realized values of sheet resistance are still one order of magnitude larger than the ones of ITO coatings, though.

3.2. *CNT thin-film transistors*

Since the low-density nanotube networks consist of individual paths rather than a bulk material, it is not only the TFT geometries which define the electrical behaviour of a single device but also the density of the network. It is therefore possible to achieve similar electrical characteristics for quite different geometries. This also means that in order to get reproducible results, the density of the nanotube network needs to be controlled very closely. Higher density networks lead to high on currents (I_{on}), but due to more metallic nanotubes also high off currents (I_{off}) and therefore a low on/off ratio (see Fig. 5). For lower density networks on/off ratios of more than five orders of magnitude were achieved on silicon wafers as well as on glass substrates. Because of the fewer current paths these devices have lower device charge carrier mobility values.

Fig. 5 shows transfer characteristics of two different devices on glass. The transfer characteristic of the low density TFT has an on/off ratio of more than 10^5, a threshold voltage of $V_{\text{th}} = -4.7\,\text{V}$ and a slope of 1.1 V/decade. Transfer and output characteristics of a device on glass are shown in Fig. 6.

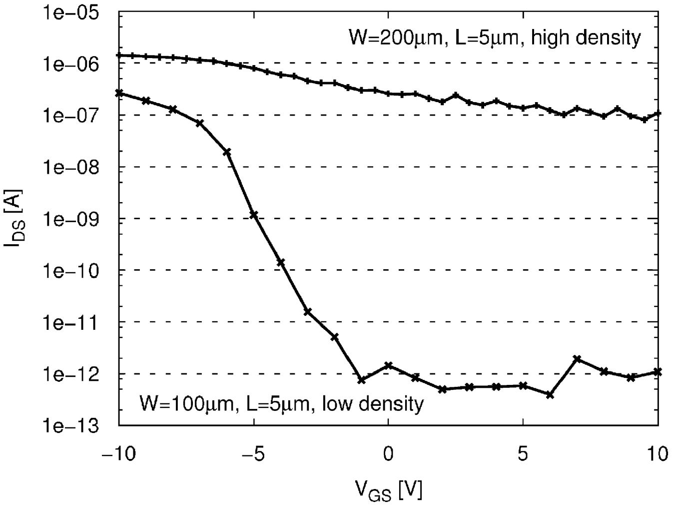

Fig. 5. Transfer characteristics of two devices on glass with different nanotube network densities.

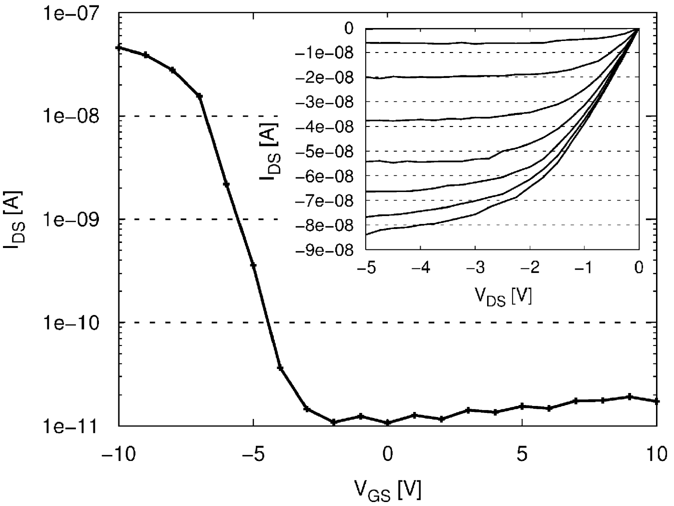

Fig. 6. Transfer and output characteristic of a device on glass with $W = 200\,\mu\text{m}$ and $L = 100\,\mu\text{m}$.

Interestingly devices with sputtered source/drain contacts (not shown) need much higher gate voltages. Presumably the nanotubes are being damaged by the impact of the accelerated metal atoms which leads to a poor contact between nanotube network and metal pad. The calculated device charge carrier mobilities on glass and wafer lie in the order of $1\,\text{cm}^2/\text{Vs}$. In the literature values of up to $150\,\text{cm}^2/\text{Vs}$ can be found for similar devices [11].

4. Conclusions

The application of nanotube networks on flexible substrates was investigated. Advantages are the low cost processes including deposition from solution, the flexibility of the produced layers and a good compatibility to plastic substrates.

The transparent and conductive coatings have very good optical performance and a sheet resistance of $400\,\Omega/\square$ can be achieved with a transmittance of 80%. This makes CNT layers a candidate for smaller, low resolution flexible displays or other applications where sheet resistances do not need to be in the order of only a few $\Omega/\square$.

The characteristics of the produced CNT-TFTs as well as the easy, low cost production make CNT network TFTs very interesting for flexible display applications and other areas where flexible electronics are needed. Efficient separation of metallic and semiconducting nanotubes would lead to a more robust process and better overall device performance. As long as metallic nanotubes cannot be removed the network density needs to be adjusted to the right compromise between high enough on-current/mobility and acceptable on/off ratio. The maximum achieved values in different devices were mobilities of more than $1\,\text{cm}^2/\text{Vs}$ and on/off ratios of more than five orders of magnitude. The main challenge, and the focus of our ongoing research work, is achieving reproducible and homogeneous results over large area substrates.

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