Flexible Electrode Formed by Patterned Layers of Single-Walled Carbon Nanotubes for Optoelectronic Applications

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Abstract. The technology of creating patterned flexible electrodes based on single-walled carbon nanotubes and polydimethylsiloxane was demonstrated in this paper. A series of experiments were carried out to study whether the percolation affects the conductivity of patterned SWCNT layers. It was found that in patterns with the linewidth above 1 µm and the cell size above 50 µm the random character of SWCNT networks may be neglected. The impact of bending on the grid conductivity was studied. We observed a very moderate increase of resistance below 5% under the strain up to 4%, which is comparable with the previous results for continuous SWCNT layers and shows the improvement in comparison with the previous reports on patterned SWCNT layers.

1. Introduction
Flexible optoelectronic device technologies have been rapidly developed in recent years. The improvement of mobile, wearable, medical, and other electronic devices imposes new requirements on their component base in terms of flexibility, stretchability, chemical stability, and service life. The flexible device technologies used today are based on organic compounds, which have fundamental limitations and some significant disadvantages: low luminosity of light-emitting diodes (LEDs), thermal and chemical instability, and relatively short service life. In turn, inorganic semiconductor compounds demonstrate high values of these parameters and are promising candidates for creating flexible and stretchable optoelectronic devices. The implementation of a flexible optoelectronic device is possible based on an array of nanowires (NWs), which are characterized by improved mechanical characteristics in comparison with bulk materials.

A typical process for flexible LEDs creating is as follows: the NWs array is filled with a layer of polymer to form a flexible matrix. After that, plasma etching is used to thin the matrix and clean the upper part of the NWs. The entire layer is then separated from the growth substrate to form a composite matrix with the NWs retaining their orientation and position. Semi-transparent and fully transparent LEDs can be manufactured using this protocol. In the case of a semi-transparent device,
the metallization of the lower part of the NW is used as the back contact. After that, the flexible substrate (for example, polyethylene terephthalate) is connected to the back metal contact with a silver epoxy resin. To create the upper electrode, an optically transparent and conductive material is used. For fully transparent LEDs, transparent conductive electrodes (TCEs) are used to create both the back and top contacts. The TCE is one of the components that significantly limits the flexibility and stretchability of LEDs.

The literature reports the use of conductive composites (silver nanowires/nanoparticles [1] or reduced graphene oxide penetrating an elastic polymer [2]), woven conductive fibers/threads [3], ionic hydrogels [4], and liquid metal [5] as flexible and stretchable electrodes. However, all of these solutions have their drawbacks. The resistance of silver nanowires increases dramatically when stretched due to the high Young's modulus. The reduced graphene oxide also loses its conductivity as it stretches. Some ionic hydrogels have good stretchability, but insufficient electrical conductivity can lead to low output characteristics of the device. Gallium-based liquid metal exhibits excellent stretchability and recyclability, but it is extremely susceptible to oxidation and has a high surface tension, which affects its fluidity and makes it difficult to use in systems with nanoscale objects.

Carbon nanotubes (CNTs) and especially single-walled carbon nanotubes (SWCNT) combining the advantages of graphene and silver nanowires, providing low cost, scalable production, simple application, and improved current collection [6]. These properties, together with anti-reflection properties and high stability, make SWCNTs one of the most promising transparent flexible, and stretchable contact materials.

Although the literature presents data on preliminary studies of SWCNT layers in optoelectronics, their potential has not yet been fully disclosed. This article is devoted to experimental work on the creation of a flexible SWCNT-based electrode for optoelectronic applications.

2. Experimental
Films of randomly oriented SWCNTs synthesized by the aerosol chemical vapor deposition (CVD) method were deposited on a nitrocellulose filter at the outlet of the reactor. We used the patterning procedure described earlier to overcome the tradeoff between conductivity and transparency [7]. Prior to patterning, the films of SWCNTs were transferred either onto a quartz substrate with pre-deposited metallic contacts or on quartz substrate with sacrificed layer for next transfer to flexible substrate.

Cr/Au (5/70 nm) contacts were deposited on quartz substrates before the SWCNT transfer by electron-beam physical vapor deposition (for Cr) and thermal evaporation (for Au) using Boc Edwards (UK) Auto 500 setup operating at 5×10⁻⁶ mbar.

After the deposition of Cr/Au contacts, the SWCNT films were transferred onto the quartz substrates, processed with isopropyl alcohol for densification and then doped in tetrachloroauric (III) acid trihydrate (HAuCl₄·3H₂O ACROS Organics) dissolved in ethanol (EtOH; 99.5%, ETAX).

The patterns of SWCNTs were produced using a combination of optical laser lithography and dry etching in an oxygen plasma. We have used the laser lithography system Heidelberg Instruments Mikrotechnik DWL 66 FS setup (Germany) with AZ MIR 701 photoresist (MicroChemicals GmbH) and AZ 726 MIF developer (MicroChemicals GmbH). The following dry etching was performed in Plasma System V 15-G (Germany) at MW-power of 400 W (O₂ flux 60 ml/min, 3 Pa) during 360 sec for 90 nm SWCNT thickness. The grids of SWCNT networks were masked by photoresist during the etching.

Unlike traditional thin films, the resistance of SWCNT stripes does not always scale linearly with the size. Thin films or narrow stripes of SWCNT networks are known to suffer from an increase of resistance due to percolation effects. Therefore, a series of experiments were carried out to study whether the percolation affects the conductivity of patterned SWCNT layers. A set of SWCNT stripes with the widths of 1-100 µm and the lengths of 10-1000 µm was prepared following the same lithography and etching procedure as described above. Figure 1 (a) shows the optical microscopy image of the SWCNT stripes with Cr/Au contacts. The resistances of SWCNT stripes were extracted
from the I-V characteristics. All the measured I-V curves have shown linear or almost linear
dependence revealing close to ohmic behavior of SWCNT-Au contact.

Figure 1 (b) and (c) shows the normalized stripe resistances $R$ as a function of the stripe length and
width correspondingly. The $R \times w$ dependences scale almost linearly (exponent about 0.95) at the
lengths above 50 $\mu$m. However, the points corresponding to the shortest measured stripes with the
length of 10 $\mu$m do not follow the linear scaling law. Previously, similar observations were attributed
to the transition from ballistic to diffusive transport in randomly oriented networks. The measured
resistances scales as $w^{-1}$ which is typical for SWCNT networks far above the percolation threshold.
Therefore, in patterns with the linewidth above 1 $\mu$m and the cell size above 50 $\mu$m the random
character of SWCNT networks may be neglected.

To make a flexible patterned SWCNT electrode and to separate it from the quartz substrate, we
used a sacrificial layer of a PMGI resist (MicroChemicals GmbH) that had been hardbaked at 200$^\circ$C
for 10 minutes. Hard bake was necessary to ensure PMGI persistence during further processing. The
continuous SWCNT layer was transferred to the hardbaked PMGI surface. Further details of the
processing, including AZ MIR photoresist spin coating, photolithography, developing, etching, and
removing the photoresist are similar to those described above. Finally, we’ve processed patterned
SWCNT electrode in geometry of square grid with cell period of 210 $\mu$m and linewidth of 20 $\mu$m.
Additional details of fabrication and characterization were discussed in [7]. After the patterned
SWCNT film was formed, the sample was poured with liquid polydimethylsiloxane (PDMS, Dow
Corning Sylgard 184) and remained in the chamber drier at 60$^\circ$C for 4 hours. After the PDMS dried,
the substrate was placed in a dimethyl sulfoxide (DMSO) solution to dissolve the sacrificial PMGI
layer. Electrical contacts to measure bending resistance were applied with silver lacquer. Figure 2 (a)
shows the view of patterned electrode on flexible PDMS substrate. The final transparency of the
electrode was 90% with resistance 200 Ohm/□.

Since flexibility is one of the most important advantages of SWCNT films, the impact of bending
on the grid conductivity was studied. During the flexibility testing the samples were bent around
quartz tubes with the diameters from 67.5 down to 22 mm. Figures 2 (b) and (c) show the sample view
sketch and the resistance variation ($\Delta R/R$) in the bend-release tests correspondingly. The strain in
figure 2 (c) was evaluated as film thickness divided by the quartz tube diameter. We observed a very
moderate increase of resistance below 5% under the strain up to 4%, which is comparable with the previous results for continuous SWCNT layers and shows the improvement in comparison with the previous reports on patterned SWCNT layers.

![Figure 2.](image)

**Figure 2.** (a) Patterned SWCNT electrode on flexible PDMS substrate. (c) Sample view sketch and (c) variation of resistance in bend-release tests.

### 3. Summary
The demonstrated technology for the fabrication of flexible patterned SWCNT electrodes can be applied to a wide range of optoelectronic devices, including flexible LEDs, thin-film solar cells or displays. A series of experiments were carried out to study whether the percolation affects the conductivity of patterned SWCNT layers. It was found that in patterns with the linewidth above 1 µm and the cell size above 50 µm the random character of SWCNT networks may be neglected. The impact of bending on the grid conductivity was studied. We observed a very moderate increase of resistance below 5% under the strain up to 4%, which is comparable with the previous results for continuous SWCNT layers and shows the improvement in comparison with the previous reports on patterned SWCNT layers.

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