Improvement of single walled carbon nanotubes layer conductivity by texturing

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Abstract. This work is aimed at finding and developing new ways to improve and optimize the characteristics of transparent conductive electrodes based on SWCNT by forming a texture in a continuous layer by combination of lithography and oxygen plasma treatment. A theoretical and an experimental justification for choosing thickness of a textured pattern, together with the experimental results of optical and electrophysical measurements were presented. The resistance of the textured electrode was 187.5 Ohm/sq, which is 17.5% lower than resistance of the electrode made from a continuous SWCNT layer with a same transparency of 95%. An analytical calculation showed that the use of extremely absorbing SWCNT films for texturing allows to obtain ~ 54% gain in the resistance of a textured electrode compared to a continuous SWCNT’s layer.

1. Introduction

The creation of new optoelectronic devices, such as solar cells, photo- and light-emitting diodes, touch screen displays, smart windows, etc., requires significant study of all aspects of their development. One of these aspects is the effective transmission or radiation output through the electrode. Although today there are various options for use as transparent electrodes, for example, a metal grids and transparent conductive oxides (TCO) based on an indium tin oxide (ITO), aluminum doped zinc oxide (AZO), fluorine tin oxide (FTO) etc., such materials cannot fully satisfy the entire spectrum of requirements imposed.

Recently, single-walled carbon nanotubes (SWCNTs) have attracted great attention of researchers due to their unique physical, electronic, optical and mechanical properties [1–4]. The growing interest in the use of two-dimensional and three-dimensional SWCNT layers is caused by the fact that such materials are promising for use in optoelectronics [5]. In addition, due to its high conductivity and optical transparency, SWCNTs can be used as an alternative to TCO and metal grids, besides SWCNTs are highly flexible [6–7]. The resistance of SWCNTs is higher than resistance of ITO at fixed transparency. 40 Ohm/sq at 90% transparency is the best value [6]. One of the ways to improve the properties of a SWCNT layers is texturing, in other words, the formation of transparent windows in a continuous SWCNT layer. A textured pattern on the surface of a SWCNT will increase the...
transparency of the existing layer, which will reduce optical losses without significantly affecting the electrophysical characteristics. Thus, the creation of a texture on the surface of SWCNTs can help to overcall a natural limitation and will allow to find the optimum between the necessary conductivity and transparency of SWCNTs. Unfortunately, to date, there is a very limited amount of information regarding the texturing of SWCNTs layers and its application as a transparent electrode in optoelectronic devices. The main task of the work was to calculate and to measure the resistance of the textured electrode (R_t) and the optical transmission of the textured electrode (T_t) created from the original continuous layer. The T_t value was chosen to be 95% which corresponds to the typical transparency of the metal contact grid used in photovoltaic converters. The resistance corresponding to a continuous SWCNT layer with 95% transmittance was also measured. The initial values of the resistance of the continuous layer (R_c) and the transmission of the continuous layer (T_c) of SWCNT from which texturing was performed were determined experimentally.

This work is aimed at finding and developing new ways to improve and optimize the characteristics of transparent conductive electrodes based on SWCNT by forming a texture in a continuous layer. The article proposes a theoretical and an experimental justification for choosing thickness of a textured pattern, together with the experimental results of optical and electrophysical measurements.

2. Calculation

The calculation of the textured electrode sheet resistance (R_t) was carried out. We assume that the unit cell of a texture has a shape of a square with the edge length A_1, linewidth half A_2 and the inner length of the edge A_3 as shown in Figure 1.

\[ T_t = \frac{A_3^2 + T_c (A_1^2 - A_3^2)}{A_1^2} = T_c + \frac{A_3^2}{A_1^2} (1 - T_c) \]  

(1)

Considering that A_3 = A_1 - 2A_2, we get:

\[ T_t = T_c + \left(1 - \frac{2A_2}{A_1}\right)^2 (1 - T_c) \]  

(2)

The model of thin stripes \((A_2/A_3 \ll 1)\) was taken for the calculation. The texture was divided into the sum of the edges connected in parallel or in series.

The resistance of the single edge is connected with sheet resistance of the continuous SWCNT layer (R_c):

\[ r = R_c \frac{A_1}{2A_2} \]  

(3)

The sheet resistance of unit cell \((R_{cell})\) is equal to \(r\) in the case of square grid.

The sheet resistance of a textured electrode \((R_t)\) can be estimated as:

\[ R_t = R_{cell} \frac{A_1}{A_3} = \frac{1}{2} \frac{A_1}{A_2} R_c \]  

(4)
Using eq. (2), we obtain the correlation between $R_t$ and $T_t$ for the textured SWCNT electrode:

$$R_t = \frac{R_c}{1 - \frac{T_t - T_c}{1 - T_c}}$$

(5)

Based on the analytical calculation and experimental $R_c$ и $T_c$ data, a graphical dependence of the transmission of the initial layer vs. sheet resistance of the textured electrode ($T_c$ vs. $R_t$) was constructed (Figure 2).

![Figure 2](image)

**Figure 2.** The dependence of the transmission of the initial SWCNT layer vs. resistance of the textured electrode.

A dependency was built for a textured layer with fixed transmission $T_t = 95\%$. Dots on the graph indicate the resistance of the textured SWCNT electrodes made from initial continuous layers with different $T_t$ and corresponding thickness. A dash line on the graph indicates the calculated resistance of the continuous SWCNT layer $R_c = 238.7$ Ohm/sq with a transparency $T_c = 95\%$.

The graph shows that with a fixed transparency of the textured layer, the least resistance will have an electrode made of a SWCNT layer with a lower base transmittance. Thus, in order to achieve the resistance value of a textured electrode with a transparency $T_t = 95\%$ lower than the resistance of a continuous SWCNT electrode with the same transparency $T_c = 95\%$, a base layer of SWCNT with $T_c < 17.4 \%$ should be used for texturing. On the graph, the «gain» area in resistance is located to the left of the intersection point of the curve «formula 1» and the dash line ($T_c = 95\%$ of reference sample). Using a texturing technique allows to reduce the resistance of the electrode compared to a continuous layer, while the transparency remains the same [7]. The use of extremely absorbing SWCNT films for texturing allows to obtain ~ 54\% gain in the resistance of a textured electrode compared to a continuous SWCNT’s layer.

3. Experimental

SWCNTs were synthesized by aerosol (floating catalyst) chemical vapor deposition and collected directly at the outlet of the reactor by deposition on a nitrocellulose filter according to the procedure described in [6]. SWCNT’s layers with different thickness ($h$) were synthesized: $h = 90, 180, 270, 360$ nm with $T_c = 63, 37.9, 25.1, 15.7 \%$ and $R_c = 27.8, 14, 9.7, 6.5$ Ohm/sq, respectively, was used to create a textured electrode. SWCNT layer with $h = 9$ nm, $T_c = 94.5\%$, $R_c =227.3$ Ohm/sq acted as a reference sample.

To form a transparent electrode, the SWCNT layer was mechanically transferred onto a quartz substrate over current-collecting contacts, followed by removal of the nitrocellulose filter. The SWCNT film was densificated with a solution of isopropyl alcohol to ensure adhesion to the surface of
the quartz. The SWCNT doping was carried out using a solution of tetrachloroauric (III) acid trihydrate in ethanol according to the procedure described in [8] to increase conductivity. The SWCNT textured electrode was fabricated using a combination of optical laser lithography and dry etching in oxygen plasma. The SWCNT conductive strips were coated with a layer of photoresist that acted as a mask for etching SWCNT. The $T_v$ value was 95%, which was realized by selecting the value of the strip width and the cell period. The experimental results of measuring the resistance and transmission of a continuous and textured electrode together with the results of an analytical calculation according to (1) are presented in the Table 1.

**Table 1.** Transparency and resistance of the continuous and textured SWCNT electrode with different thickness.

| h, nm | $T_v$ (analytic), % | $T_v$ (experiment), % | $R_c$ (analytic), Ohm/sq | $R_c$ (experiment), Ohm/sq | $T_t$ (analytic), % | $R_t$ (analytic), Ohm/sq | $R_t$ (experiment), Ohm/sq |
|-------|---------------------|-----------------------|---------------------------|---------------------------|---------------------|---------------------------|---------------------------|
| 9     | 95.0                | 95.0                  | 227.3                     | —                         | —                   | —                         | —                         |
| 90    | 60.0                | 63.0                  | 27.8                      | 95.2                      | 389.3               | 414.4                    |
| 180   | 36.0                | 37.9                  | 14.1                      | 95.3                      | 315.5               | 334.2                    |
| 270   | 21.6                | 25.1                  | 9.7                       | 94.7                      | 260.4               | 233.4                    |
| 360   | 12.7                | 15.7                  | 6.5                       | 94.7                      | 215.9               | 187.5                    |

The data presented in the Table 1 shows that the results of experimental sheet resistance and transparency measurements and data of analytical calculation have a good correlation. The experimental measurement resistance value of the textured electrode with $h = 360$ nm was $R_t = 187.5$ Ohm/sq, which is 17.5% lower than continuous layer SWCNT electrode ($R_t = 227.3$ Ohm/sq) with a similar transparency. Fabrication of a textured electrode from continuous layers with even lower $T_v$ transmittance and $R_c$ resistance will give a greater gain in $R_t$ resistance. The analytical calculation data and experimental results show a good correlation. The reduced values of the experimental resistance $R_t$ compared to the calculated $R_t$ values are due to the lower experimental transmittance $T_t$ (94.7% in the experiment and 95% in the calculation).

4. **Summary**

The demonstrated technology for the fabrication of textured SWCNT electrodes can be applied to a wide range of optoelectronic devices, including flexible thin-film solar cells or displays. SWCNT textured electrode showed lower resistance compared to the continuous SWCNT layer with same transparency. To achieve maximum conductivity of the textured electrode, it is necessary to use SWCNT with the lowest base transmission for its fabrication. The calculated resistance of the continuous layer SWCNT electrode with 95% transparency is 238.7 Ohm/sq, while the resistance of a textured SWCNT electrode with the same transparency reaches a value of 215.9 Ohm/square and over. The experimental measured resistance of the continuous layer SWCNT electrode with 95% transparency is 227.3 Ohm/sq, while the resistance of a textured SWCNT electrode with the same transparency is 17.5% lower and equal to 187.5 Ohm/square. An analytical calculation showed that the use of extremely absorbing SWCNT films for texturing allows to obtain ~ 54% gain in the resistance of a textured electrode compared to a continuous SWCNT’s layer.

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