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Scanning Electron Microscopy of Semiconducting Nanowires at Low Voltages

Tomas TAMULEVIČIUS[1,2*], **Asta ŠILEIKAITĖ**[1], **Sigitas TAMULEVIČIUS**[1,3],
Morten MADSEN[4], **Horst-Günter RUBAHN**[4]
[1]*Institute of Physical Electronics of Kaunas University of Technology, Savanorių av. 271, LT-50131, Kaunas, Lithuania*
[2]*Faculty of Design and Technologies, Kaunas University of Technology, Studentų str. 56, LT-51424 Kaunas, Lithuania*
[3]*Department of Physics, Kaunas University of Technology, Studentų str. 50, LT-51368 Kaunas, Lithuania*
[4]*University of Southern Denmark, Mads Clausen Institute, NanoSYD, Alsion 2, Sønderborg DK-6400, Denmark*

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Light emitting para-hexaphenylene (p6P) nanofibers with typical widths of a few hundred nanometers and heights of a few ten nanometers are analyzed with the help of a field emission scanning electron microscope (FESEM). Charging effects are minimized by transferring the nanofibers onto silicon substrates and by applying very low acceleration voltages in the FESEM, down to 100 V. The resulting measured planar dimensions of the nanofibers (length and width) agree qualitatively with those measured by atomic force microscopy. At very low voltages the FESEM images also reveal significantly more detailed information from the surface of the nanofibers as compared to measurements performed at more conventional, high voltages of kilovolts. However, with increasing electron dosage charging and radiation-induced modification of the nanofibers is observed, leading to an apparent increase of width and length. We interpret this increase as being due to electron-induced polymerization at the interface between nanofibers and substrate.

Keywords: organic nanofibers, para-hexaphenylene (p6P), FESEM characterization.

1. INTRODUCTION

Conjugated oligomer molecules such as α-thiophenes, oligoacenes, para-phenylenes, or phenylene/thiophene co-oligomers are supposed to play an important role in future electronic and optoelectronic devices. Choosing the right combination of organic adsorbate and inorganic or organic substrate, aggregates such as nanofibers or microrings can be assembled by a bottom-up growth process [1]. Para-hexaphenylene (p6P) nanofibers formed by molecular beam epitaxy have different dimensions in different directions, viz. macroscopic length (up to millimeters) but nanoscopic width (hundreds of nanometers) and height (several ten nanometers). Linear dimensions of the organic nanofibers can be important for their electrical, mechanical and optical properties. In general, organic nanofibers as a new kind of nanoscaled materials possess interesting optical [2, 3], mechanical [4] and electrical properties [5, 6]. They can be grown from simple oligophenylenes, but also from functionalized molecules that are generated with the help of synthetic chemistry [7]. For blue-light emitting devices, the para-phenylenes and, especially p6P with its high quantum efficiency and thermal and chemical stability are of special interest.

Previously organic nanofibers have been investigated employing scanning near field microscopy [8], atomic force microscopy (AFM) [1 – 7, 9 – 11] and to a much lesser extent scanning electron microscopy (SEM) [5 – 6, 9, 12]. In the latter work [12] the SEM was used to investigate the manipulation of the fibers done with a scanning tunneling microscope (STM). Note that the nanofibers are made of a high band gap semiconductor and behave similar to a dielectric as concerns their response to electron irradiation. This results in very strong charging effects, which in turn make it impossible to obtain detailed surface or correct morphologic information from scanning electron microscopy measurements.

In this work we investigate whether it is possible to obtain high resolution structural surface information from FESEM measurements by implementing very low accelerating voltages down to 100 V. By comparing the linear dimensions of the nanofibers using AFM measurements before and after SEM treatment we deduce that the nanofibers grow with an increase in electron dosage by an electron-induced polymerization process.

2. EXPERIMENTAL

2.1. Formation and transfer of the nanofibers

Nanofibers from p6P molecules were grown on freshly cleaved muscovite mica ($K_2Al_4[Si_6Al_2O_{20}](OH)_4$) substrates (that develops surface dipole field of the order of 10^7 V/cm [13]) using an OMBE (organic molecular beam epitaxy) apparatus with a Knudsen effusion cell. The growth process (i. e. the impinging flux of molecules) was monitored using a water-cooled quartz microbalance. Deposition occurred at a typical rate of ~0.1 Å/s – 0.2 Å/s under a dynamic vacuum of ~10^{-5} Pa, at a substrate temperature of about 420 K. Sublimation from the Knudsen cell took place at a temperature of approximately 650 K. Mutually aligned nano-aggregates (fibers or needles) formation is caused by the substrate and p6P molecules dipole-induced dipole interactions leading to oriented growth of the molecules in the initial deposition phase [2, 10].

On the other hand, mica samples are insulators and cause charging effects while imaging organic nanofibers with SEM. To avoid charging effects from the substrate, the fibers were transferred onto a crystalline silicon substrate [11] employing a transfer liquid and

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[*]Corresponding author. Tel.: +370-37-313432; fax: +370-37-314423.
E-mail address: *t.tamulevicius@stud.ktu.lt* (T. Tamulevičius)

implementing a soft contact between mica and silicon substrates.

2.2. Analytical techniques

The following analytical techniques were used to characterize linear dimensions and morphology of the p6P nanofibers: optical/fluorescence microscope Nikon, AFM JPK NanoWizard, FESEM Hitachi S-4800. The targeted place on the sample with nanofibers was found employing an AFM on top of an inverted fluorescent microscope (a high pressure mercury lamp was used for the excitation $\lambda = 365$ nm) and top-view optics placed on an active vibration table (Halcyonics GmbH). As the silicon substrate is not transparent, the sample in the AFM was observed with a top-view optics in reflection using a CCD camera and a long distance top-view optics. The FESEM Hitachi S-4800 (magnification: ×30 – ×800,000) used in the experiment employs a conventional semi-in-lens design for accommodating large samples (with 110 mm × 110 mm movement and computer controlled motorized 5 axes (*X*, *Y*, *Z*, *R*, *T*)), advanced dry vacuum system design (including three Ion pumps (IP), Turbo Molecular Pump (TMP) and rotary pump (RP)), and can be used to achieve ultra-high spatial resolution of a few nanometers. The SEM uses a single in lens detector ("Super ExB Filter") that collects and separates the various components of pure secondary electrons (SE), compositional SE and backscattered (BSE) electron signals. Using a de-acceleration function it is possible to obtain images down to an effective 0.1 kV accelerating voltage.

3. RESULTS AND DISCUSSIONS

Fluorescence microscope images reveal a dense film of well aligned nanofibers as grown on a mica substrate (Fig. 1).

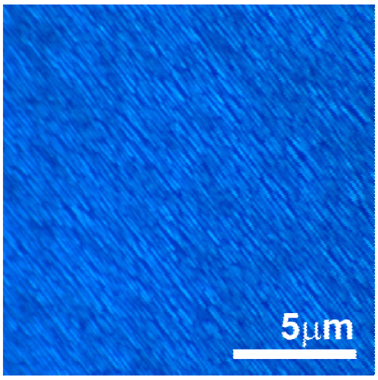

Fig. 1. Fluorescence microscope image of p6P nanofibers grown on muscovite mica (coloured online)

After growth, the nanofibers were transferred onto the Silicon substrates, on which they were analyzed by SEM. By using the de-acceleration function on the SEM, the nanofibers were imaged with low voltages at the sample site ranging from 0.1 kV to 0.6 kV. This was done by using accelerating voltages from 1.6 kV to 2.1 kV and then a de-accelerating voltage of 1.5 kV. Typical results are shown in Fig. 2.

As seen on the images, charging effects are minimal at 0.1 kV, but become visible already at 0.3 kV (white areas around the fibers). This is seen more clearly in Fig. 3, which shows a zoom-in on the images from Fig. 2. Note that at very low voltages surface structures become visible, that are blurred at higher voltages. The main reason for that are minimized charging effects; however, the penetration depth of the imaging electrons is also decreased by decreasing the effective voltage.

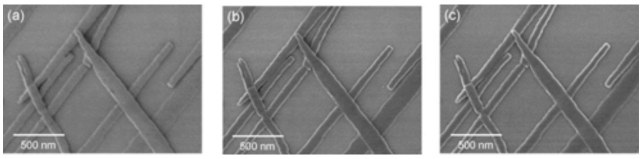

Fig. 2. SEM images of transferred p6P nanofibers on silicon (SE signal). The voltages at the substrate were a – 0.1 kV, b – 0.3 kV and c – 0.6 kV. The nanofibers have been imaged with a magnification of 50 000

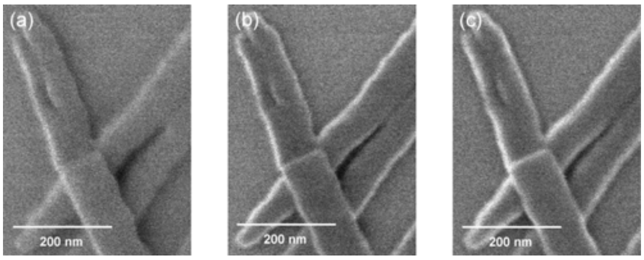

Fig. 3. Same as Fig. 2, but zoom-in

Using low voltages it becomes also possible to detect the presence of different surface layers, induced by the transfer process of the nanofibers. This is shown in Fig. 4, a, where two separated nanofibers have been imaged with a voltage of 0.2 kV. When the voltage is increased to 1.0 kV, this layer is no longer seen on the image, Fig. 4, b. At this voltage, the nanofibers also charge up as it was shown before. Note that this voltage has a destructive effect on the surface layer, so it is not possible to detect the layer again when resetting the voltage back to 0.2 kV, Fig. 4, c. Furthermore, charging is still present when changing the voltage back to 0.2 kV.

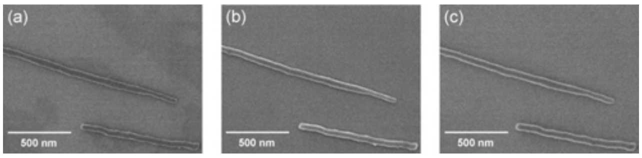

Fig. 4. SEM images of p6P nanofibers on silicon (SE signal). The applied voltages were: a – 0.2 kV, b – 1.0 kV and c – 0.2 kV. The nanofibers have been imaged with a magnification of 40 000

Although there is only very little charge build-up when using a voltage of 0.2 kV, one still changes the structure of the nanofibers by scanning a certain area too long. This is shown in Fig. 5, where the electron beam exposure time is increased from below a minute (Fig. 5, a) to 10 minutes (Fig. 5, b) and 20 minutes (Fig. 5, c). The voltage is kept constant at 0.2 kV. Note that the nanofibers appear bigger when the exposure time is increased. This is probably a combination of both charge build-up and electron-induced polymerization.

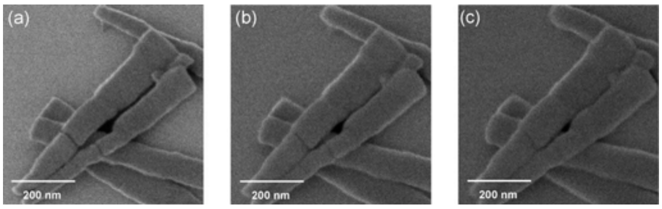

Fig. 5. SEM images of p6P nanofibers on Silicon (SE signal). The area has been scanned for a – below a minute, b – 10 min. and c – 20 min. The voltage was 0.2 kV. The nanofibers have been imaged with a magnification of 50 000

To elucidate possible effects of charge or polymerization we have investigated more systematically linear dimensions of the nanofibers using simultaneously AFM and SEM. A group of separated fibers was chosen (see Fig. 6). AFM profiles were deconvoluted from tip artefacts (Fig. 7) using the Gwyddion software [14]. From averaged line scans of the nanofibers, linear dimensions of the fibers (indicated with numbers from P1 to P8) were obtained (see Table 1).

Widths and lengths of the fibers were measured several times at the same place and at the same conditions, but different magnifications or scanning areas were used. For every analysed nanofiber (P_i, $i = 1-8$) we have calculated the standard deviation (STDEV) of the linear dimensions:

$$STDEV = \sqrt{\frac{\sum_i \left(x_i - \bar{x}\right)^2}{(n-1)}}\,; \qquad (1)$$

here, x_i is the i-th measured value, $\bar{x}$ is the average value, n is the total number of the measurements taken at the same place in different AFM or SEM pictures.

After the AFM analysis the sample was investigated with the SEM at the same place using the de-acceleration function and varying accelerating voltages from 0.1 kV to 0.4 kV in increments of 0.1 kV. Averaged linear dimensions and corresponding standard deviation values are presented in Table 2. After the SEM investigation the AFM measurements were performed again (see Table 1 and Fig. 8).

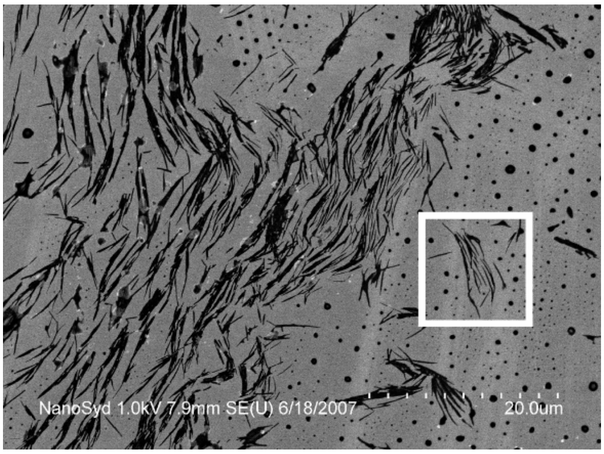

Fig. 6. SEM image of the nanofibers transferred onto Si (SE signal). The white square indicates the fibers analyzed with AFM

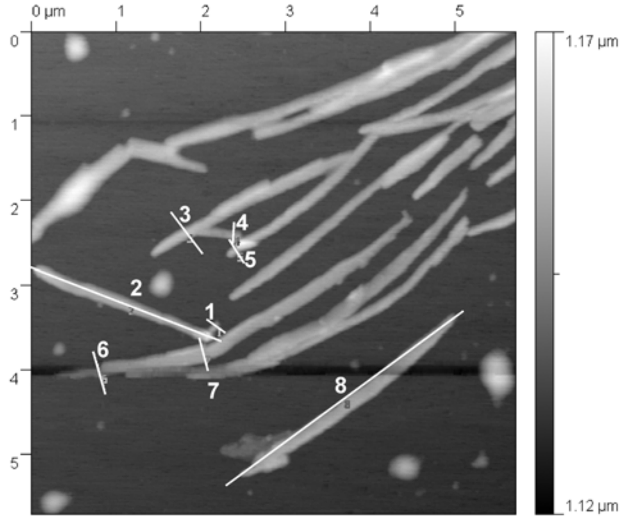

Fig. 7. Deconvoluted AFM image of the p6P nanofibers transferred onto silicon. Numbers (1 – 8) and lines indicate where the cross-sections were measured with AFM and compared with the SEM measurements

Table 1. Widths (w) and lengths (l) of the nanofibers registered with AFM before and after using the SEM

	Before SEM		After SEM		
	Width, length [nm]	STDEV [nm]	Width, length [nm]	STDEV [nm]	Absolute difference (increase) [nm]
P1	117.30 (w)	4.45	154.75 (w)	4.89	37.45
P2	2310.00 (l)	10.00	2340.00 (l)	14.14	30.00
P3	190.32 (w)	1.06	202.68 (w)	3.38	12.36
P4	148.02 (w)	1.66	154.39 (w)	0.74	6.37
P5	157.39 (w)	1.75	190.81 (w)	0.52	33.42
P6	158.73 (w)	0.35	169.14 (w)	0.93	10.40
P7	257.96 (w)	3.41	263.82 (w)	2.99	5.85
P8	3216.67 (l)	11.55	3240.00 (l)	–	23.33

Table 2. Dimensions of the nanofibers registered with SEM (BSE) at different accelerating voltages. Values above 2000 nm refer to lengths, smaller values to widths

	0.1kV		0.2kV		0.3kV		0.4kV	
	D [nm]	STDEV [nm]	D [nm]	STDEV [nm]	D [nm]	STDEV [nm]	D [nm]	STDEV [nm]
P1	45.8	1.8	55.4	4.4	72.1	4.8	78.2	2.8
P2	2092.5	10.6	2092.6	3.3	2146.0	–	2174.4	3.7
P3	86.5	3.5	96.0	–	98.2	2.6	119.4	2.0
P4	51.9	–	58.3	–	72.0	0.0	75.4	0.5
P5	69.0	–	83.0	2.0	87.9	4.0	102.2	4.0
P6	62.0	4.2	69.0	–	76.0	–	90.5	3.6
P7	181.1	1.3	183.4	2.3	191.5	4.9	216.3	5.0
P8	3023.0	–	–	–		–	3103.0	–

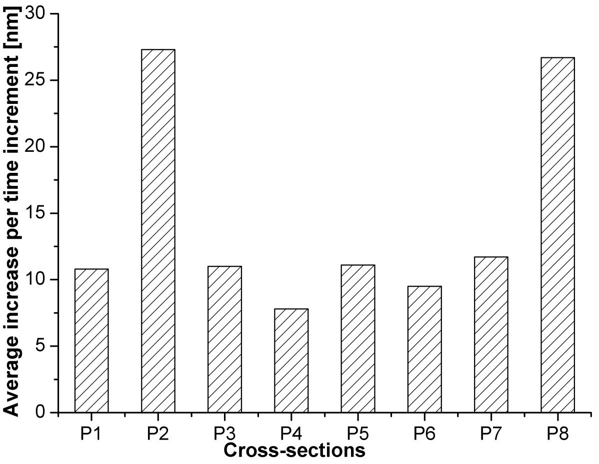

Fig. 8. Average increase per time increment of nanofiber dimensions following SEM irradiation for different fibers (Table 2). For samples 2 and 8 the increase in length, for all others the increase in width has been plotted

Changes of the linear dimensions due to the irradiation with electrons were evaluated by the AFM. The resulting values are also given in Table 1. The AFM results shown in Table 1 are in a good agreement with the previously stated results (Fig. 5) that there is a small increase of the linear dimensions (widths and lengths) after electron irradiation of the order of 10 nm to 30 nm (while height increasing up to 1 nm – 2 nm). That might result from electron induced polymerization of the p6P molecules [12] as well as possible polymerization from the carbon tape used to mount the sample in the SEM.

The dimensions of the nanofibers (length or width noted as D) increase also with increasing electron irradiation dose, as demonstrated in Table 2 and Fig. 8. Here, the same areas on the sample were irradiated under different effective voltages for a continuous exposition time of approximately 3 hours. In total we have taken 50 pictures of the same place (giving higher exposition dose then just viewing the sample surface on the screen) while the emission current was changing in the range of 5.8 μA – 12.5 μA. It is seen that for given time increment of electron exposure the width is increasing by approximately 10 nm, while the length is increasing by approximately 27 nm. Note that the crystalline structure of the nanofibers results in different slopes at the sides and at the tips of the nanofibers, respectively. Thus while the volume increase in material at the tips and at the sides might be the same, the linear dimensions could grow differently.

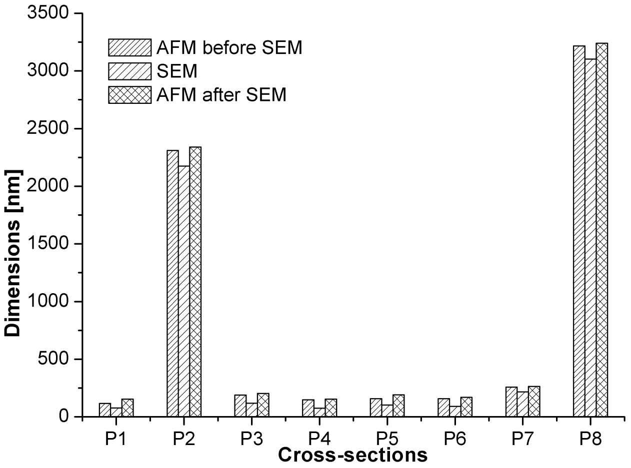

Fig. 9. Comparison of the nanofiber dimensions registered with AFM (before and after SEM) and SEM (results when accelerating voltage was 0.4kV)

The observation that the dimensions registered with AFM in general are larger than those registered with SEM (Fig. 9) might be traced back to tip artefacts in the AFM evaluation. Remaining charging effects in the SEM are another source of uncertainty regarding determination of absolute dimensions.

4. CONCLUSIONS

In this article we have systematically investigated whether it is possible to obtain reliable quantitative morphologic data from dielectric or semiconducting nanoaggregates using scanning electron microscopy. Charging effects have been minimized by transferring the nanofibers onto crystalline silicon substrates and by applying very low acceleration voltages in the FESEM, down to 100 V. The resulting measured planar dimensions of the nanofibers (length and width) are systematically smaller than those measured by atomic force microscopy, an observation which is traced back to tip artefacts. At very low voltages the FESEM images reveal more detailed information from the surface of the nanofibers as compared to measurements performed at more conventional, high voltages of kilovolts. However, with increasing electron dosage charging and radiation-induced modification of the nanofibers is observed, leading to an apparent increase of width and length. Quantitatively, the length seems to increase more than the width, which might be traced back to the crystalline packing of the nanofibers. In general we interpret the electron induced increase as being due to polymerization at the interface between nanofibers and substrate.

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