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Morphology and composition of silica nanowires synthesized on indium and tin catalysts

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Abstract. Silicon nanowires were synthesized by electron beam plasma-enhanced chemical vapor deposition. The synthesis was carried out using indium and tin catalyst with an average particle size of 100 and 660 nm, respectively, in the temperature range 100-270 °C for indium and 200-335 °C for tin. The minimum (optimum) temperature was found at which an oriented array of microropes was formed. This temperature was 200 °C for indium and 335 °C for tin. In addition, it was found that the formation of individual microropes on the tin catalyst occurred at a temperature lower than the eutectic temperature (232 °C). For indium, this effect was not observed. The silica nanowires synthesized on both catalysts consist of SiOx with x ranging from 1.9 to 2 for all temperatures.

1 Introduction

Materials with reduced dimensionality (1D or 2D) have attracted considerable interest due to their unique properties and promising applications in photonic and photovoltaic devices, sensors, catalyst supports, etc. [1-3]. In particular, silica nanowires with developed surface have a great potential for use in such devices. In addition, these nanowires have diverse and fairly simple morphology. They are easily modified and functionalized by applying thin films and decorating with metal nanoparticles [2, 3]. These nanostructures are used in lithium-ion batteries and solar cells.

In this study, silica nanowires were synthesized on indium and tin catalysts by gas-jet electron beam plasma-enhanced chemical deposition according to the vapor-liquid-crystal mechanism. The purpose of this work was to study the morphology and composition of nanostructures as a function of synthesis temperature and catalyst type. In addition, it was necessary to determine the minimum (optimum) temperature at which the synthesis of oriented microropes occurred. This would allow the use of inexpensive low-temperature substrates to simplify the manufacture of devices based on nanowires.

2 Experimental

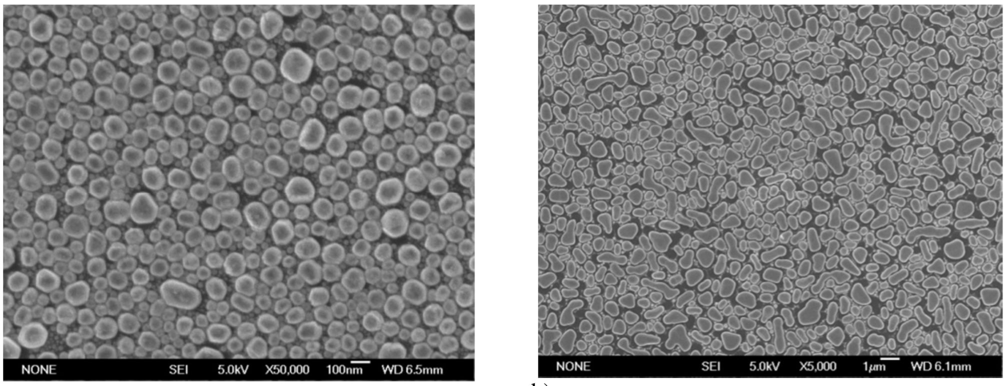
Silicon nanowires were synthesized on indium and tin catalysts by gas-jet electron beam plasma-enhanced chemical vapor deposition [4] according to the vapor-liquid-crystal mechanism. The synthesis was carried out in a vacuum chamber evacuated to a pressure of

6 Pa. During the process, the pressure rose to 20 Pa. The working gases were hydrogen, a mixture of 5% monosilane in argon, and oxygen. The gas flow rate was 386 sccm for hydrogen, 36 sccm for the monosilane-argon mixture, and 6 sccm for oxygen. The vacuum chamber was equipped with a plasma-cathode electron gun. The gun produced an electron beam with an energy of 600 eV and a current of 50-70 mA. Single-crystal (100) silicon wafers were used as substrates for the synthesis. The indium or tin catalyst was deposited on the substrates by thermal vacuum deposition. The nanowire synthesis process can be divided into three stages: heating of the substrate with the catalyst to operating temperature, hydrogen plasma treatment, and proper synthesis. The catalyst was treated with hydrogen plasma for 5 min, after which a monosilane-argon mixture was added to the hydrogen (without stopping the process and breaking the vacuum) and the growth of nanostructures was carried out for 10 min. The synthesis temperature for the indium catalyst was varied from 100 to 270°C, and for the tin catalyst from 200 to 335 °C.

The morphology of the synthesized nanostructures was investigated using a JEOL JSM-6700F scanning electron microscope equipped with an energy dispersive spectrometer (EDS). To Chemical composition was studied by Fourier transform infrared (FTIR) spectroscopy using a Scimitar FTS 2000 spectrometer in the range from 4000 to 400 cm-1 with a resolution of 1 cm-1.

3 Result and discussion

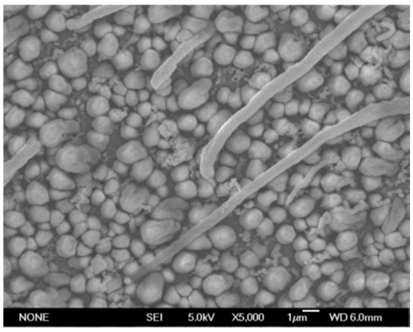
The indium and tin catalysts used for the synthesis of silica nanowires were prepared by thermal vacuum deposition. SEM images of the catalysts presented in Figs. 1a and 1b show that both catalysts are island films. According to the size distribution functions obtained for these catalysts, the mean particle size is 100 nm for indium and 660 nm for tin. This choice of particle sizes of the catalysts is based on experimental data showing that indium particles with a size of 80-100 nm and tin particles with a size of 400-700 nm are best suited for the synthesis of oriented arrays of microropes.



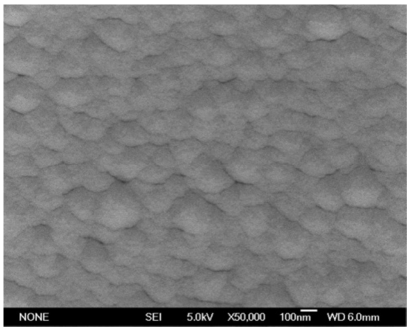
a) b)

Fig. 1. SEM image of the catalysts for the synthesis of silica nanowires: a) indium, b) tin.

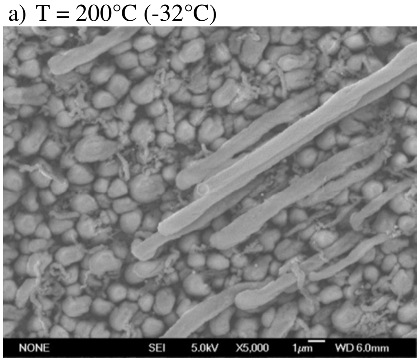
Two series of experiments on the synthesis of silica nanowires on indium and tin catalysts were performed. The growth of all nanowires on both catalysts occurred under identical conditions, except for the temperature range. Figure 2 shows a comparison of SEM images of the nanowires.



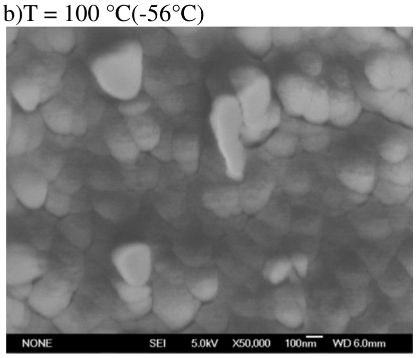
a) T = 200°C (-32°C)



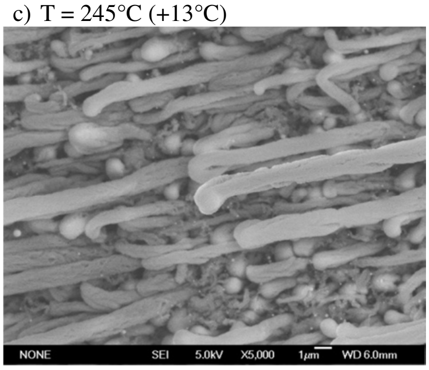
b)T = 100 °C(-56°C)



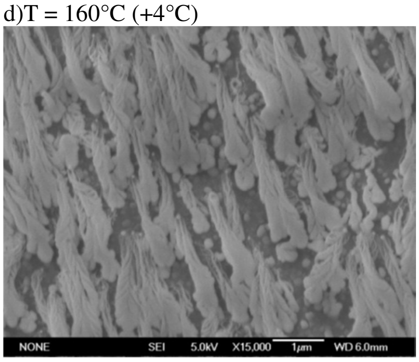
c) T = 245°C (+13°C)



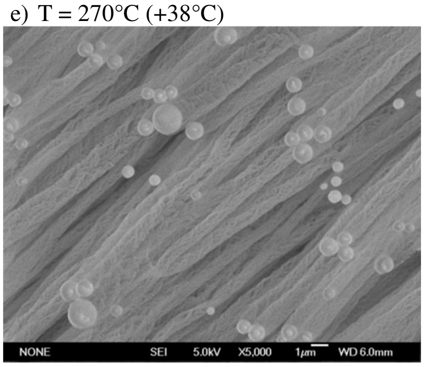
d)T = 160°C (+4°C)



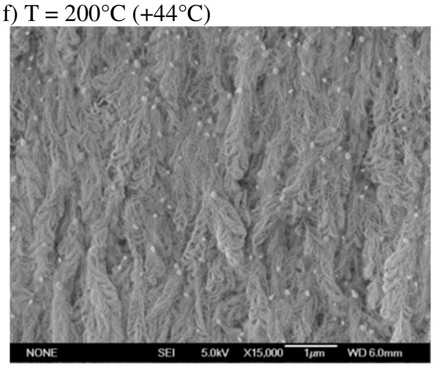
e) T = 270°C (+38°C)



f) T = 200°C (+44°C)



g) T = 335°C (+103°C)



h) T = 245°C (+89°C)

Fig. 2. SEM images of the silica nanowire structures grown on the tin (left) and indium (right) catalysts at temperatures of (a) 200 °C, (b) 100 ° C, (c) 245 °C, (d) 160°C, (e) 270 °C, (f) 200 °C, (g) 335°C, (h) 245 C. (The synthesis temperature is indicated under each image, and the difference between the synthesis temperature and the eutectic temperature is given in parentheses.

We compared nanostructures for which the differences between the synthesis temperature and the eutectic temperature were approximately equal. The eutectic temperature for the indium-silicon alloy is 156 C, and that for the tin-silicon alloy is 232 °C. At a temperature below the eutectic temperature cocoon-like structures and individual microropes similar to those described in [5, 6] were formed on the tin catalyst (Fig. 2a), and a SiOx film was obtained on the indium catalyst (Fig. 2b).

Figure 2c and 2d shows SEM images of nanowires grown at a temperature slightly higher than the eutectic temperature. It is seen that on the tin catalyst at a temperature of 245 °C (Fig. 2c), in addition to numerous cocoon-like structures, individual microropes are formed and they are more abundant than at a temperature of 200 °C. On the indium catalyst at a temperature of 160 °C (Fig. 2d), only cocoon-like structures were formed.

Figure 2e and 2f shows a comparison of SEM images of nanostructures grown at temperatures approximately 40 °C higher than the eutectic temperature. On the tin catalyst (Fig. 2e), one can see cocoon-like structures and individual microropes even more abundant than at lower temperature. At a temperature of 200 °C (Fig. 2f), an oriented array of microropes is formed on the indium catalyst, i.e., this temperature is optimal for the indium catalyst.

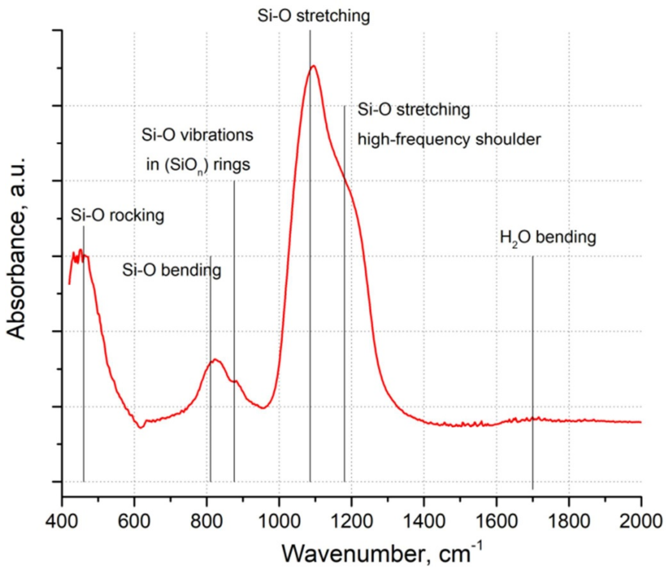


Fig. 3. FTIR spectrum for silica nanostructures grown on the indium catalyst at a temperature of 245°C.

Figure 2g and 2h shows a comparison of SEM images of nanostructures grown at a temperature approximately 90 °C higher than the eutectic temperature. The synthesis of nanostructures on tin at a temperature of 335 °C (Fig. 2g) resulted in an oriented array of microropes. The diameter of this microrope is approximately equal to the size of the catalyst particle. Thus, 335 °C is the optimal temperature for the tin catalyst. The microropes grown on the indium catalyst at a temperature of 245 °C (Fig. 2h) are fluffy, not very well oriented, and form something resembling a feather.

FTIR spectra were obtained to study the composition of nanostructures synthesized on the indium and tin catalysts. All these spectra are identical, except for the intensity and slight displacement of the peaks. Figure 3 shows a typical FTIR spectrum for nanowires synthesized on the indium catalyst at a temperature of 245 °C. The main features of the

FTIR spectrum are the Si-O asymmetric stretching mode (main peak) and the Si-O symmetric stretching mode (high-frequency shoulder). This indicates that nanowires are composed of SiOx. According to [7], the stoichiometric coefficient x is directly proportional to the position of the Si-O stretching band under the assumption of a uniform distribution of silicon and oxygen atoms in the SiOx material. With this assumption, it is found that for nanowires synthesized on the indium and tin catalysts at all temperatures, the stoichiometric coefficient is in the range from 1.9 to 2.

4 Conclusions

Silicon nanowires were grown on indium and tin catalysts by gas-jet electron beam plasma-enhanced chemical deposition. The change in nanostructure morphology was studied in the range 200-415 °C for nanowires synthesized on the tin catalyst and in the range 160-335 °C for nanowires synthesized on the indium catalyst. The optimum temperature for the synthesis of an oriented array of microropes of nanowires was found. For the tin catalyst, this temperature is 335 °C, and for the indium one, 200 °C. At a temperature below the tin-silicon eutectic temperature (232 °C), individual microropes of nanowires are formed, whereas for indium, this is not the case. It is established that silica nanowires consist of SiOx with x in the range from 1.9 to 2 for all temperatures, assuming a uniform distribution of silicon and oxygen atoms.

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