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Effect of indium catalyst particle size on the morphology of silicon oxide nanowires

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Abstract. Silicon oxide (SiO$_x$, $x \leq 2$) nanowires were synthesized on indium (In) catalyst particles by gas-jet electron beam plasma-enhanced chemical vapor deposition through the vapor-liquid-solid (VLS) mechanism. The synthesis was carried out on substrates of different average particle sizes in the range from 42 to 710 nm. Arrays of oriented microropes of nanowires were grown on catalysts with a particle size of 42 and 79 nm. On 170 nm catalyst particles, cocoon-like structures from nanowires were formed, and on 710 nm particles, the synthesis proceeded in the same way as on an indium tin oxide (ITO) film. The chemical composition of the synthesized nanostructures was studied by Fourier transform infrared spectroscopy. Under the assumption of a uniform distribution of silicon and oxygen atoms, the nanowires were found to consist of SiO$_x$ with $x = 1.9$. Energy dispersive spectroscopy showed that the catalyst particles consisted of non-stoichiometric indium oxide, rather than of pure indium. Therefore, during the synthesis of silicon oxide nanowires on an indium catalyst, hydrogen should be used.

1. Introduction
Due to their unique properties, one-dimensional structures such as nanowires and nanotubes are of great fundamental interest and have great potential for application in photonics, photovoltaics, power engineering, as chemical and biological sensors, etc. [1–3]. In particular, silicon oxide (SiO$_x$) nanowires are characterized by stable blue photoluminescence at room temperature [4], low refractive index [5], and small absorption coefficient. In addition, these nanowires have diverse and modifiable morphology. They are easily functionalized by applying thin films and decorating with metal nanoparticles [2, 3]. These nanostructures are used in lithium-ion batteries and solar cells.

Typically, silicon oxide nanowires are grown on single-crystal silicon substrates coated with a thin metal film by thermal evaporation method through the VLS mechanism. The substrate is a source of silicon atoms. Naturally, this method has significant drawbacks such as high temperature (about 1100°C) [3, 6] and long synthesis time. Using plasma-enhanced chemical vapor deposition [7] eliminates these drawbacks, but, in this case, low-melting metals should be used as catalyst. The most common metals for the synthesis of silicon oxide nanowires are gold, tin, and indium. Among them, indium has the lowest eutectic temperature (157°C). The low temperature makes it possible to use inexpensive low-temperature substrates (for example, glass), which reduces the cost of the synthesis and allows the fabrication of devices.
In this study, silicon oxide nanowires were synthesized on an indium catalyst by gas-jet electron beam plasma-enhanced chemical deposition through the vapor-liquid-crystal mechanism. The purpose of this work was to investigate the synthesis of nanowires, including oriented arrays, and their properties using catalysts with an average particle size of 30 to 710 nm.

2. Experimental
Silicon oxide nanowires were synthesized on an indium catalyst by gas-jet electron beam plasma-enhanced chemical vapor deposition through the vapor-liquid-crystal mechanism. A description of the method can be found in [8]. The synthesis was carried out in a vacuum chamber evacuated to a pressure of 6 Pa. During the process, the pressure increased to 20 Pa. Hydrogen, a mixture of 5% monosilane in argon, and oxygen were used as working gases. 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 an electron gun with a plasma cathode. This gun produces an electron beam with energy of 600 eV and current of 50-70 mA. Single-crystal (100) silicon wafers were used as substrates. An indium catalyst film of different mass thickness was deposited on the substrates by thermal vacuum deposition. The nanowire synthesis processes can be divided into three stages: heating 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 (without stopping the process and breaking the vacuum) was added to hydrogen and the growth (synthesis) of the nanostructures occurred for 10 min. The substrate (synthesis) temperature in all the experiments was 200°C. This temperature was chosen because this is the minimum temperature at which arrays of oriented microropes of nanowires were formed [9, 10].

The morphology of the synthesized nanostructures was investigated using a JEOL JSM-6700F scanning electron microscope equipped with an energy dispersive spectrometer (EDS). For chemical composition analysis, Fourier transform infrared (FTIR) spectra were recorded on a Scimitar FTS 2000 spectrometer in the range from 4000 to 400 cm$^{-1}$ with resolution of 1 cm$^{-1}$.

3. Result and Discussion
Catalysts with different particle sizes were prepared by thermal vacuum deposition. SEM images of the catalysts are presented in Fig. 1. It is seen that the catalyst is a discontinuous (island) film, with individual particles exhibiting typical crystal faces. Distribution functions were obtained, according to which the average particle size is 42, 79, 170, and 710 nm, respectively.
Figure 2 shows SEM images of silicon oxide nanowires synthesized on indium catalyst particles of different sizes at a temperature of 200°C. Figure 2a shows silicon oxide nanostructures synthesized on an indium catalyst with an average particle size of 42 nm. It can be seen from the figure that microropes of nanowires are formed on individual catalyst particles, and these microropes are similar to the structures formed on a tin catalyst in [11]. The array of these microropes has a preferred direction, although some microropes are curved and turned aside and the distance between nanowires in them is increased. It can also be seen that some microropes are markedly thickened in the lower part. Catalyst particles are at the top of microropes and have a spherical shape. This may be due to the fact that the catalyst particles were in the liquid state during the synthesis. With an increase in the average particle size of the catalyst to 79 nm (Fig. 2b), the array of microropes becomes more oriented, the distance between nanowires in a microrope is markedly decreased, and the size of the lower part of the microrope does not change. With a further increase in the particle size of the catalyst to 170 nm (Fig. 2c), cocoon-like nanowire structures are formed, similar to those described in [11]. Among these structures, separate microropes can be seen. And finally, each of the catalyst particles with an average size of 710 nm is overgrown with an array of microropes as a result of the synthesis (Fig. 2d). At the tops of these microropes, there are small catalyst particles (about 30 nm). Note that the size of the catalyst particles at the tops of microropes in Fig. 2c is about 10 nm. In both cases, this size does not correlate with the size of the original catalyst. At the same time, the size of the catalyst particles in Figs. 2a and 2b is about 60 nm and 100 nm, respectively, which is consistent with the size of the original catalyst particles.

The morphology of these structures from nanowires can be explained by the synthesis model proposed in [10, 11]. According to this model, the nanowires were grown bottom-up on indium catalyst particles by the VLS process. After the start of the synthesis, silicon-containing radicals, which have a sufficient lifetime, are transferred by the jet to a catalyst particle. They enter the particle to form an eutectic melt. Oxygen enters the catalyst particle from the vacuum chamber. Supersaturation of the eutectic melt results in the formation of nuclei and nanowires. Directed synthesis of nanowires with the formation of microropes is due to the influence of the plasma flow, which leads to uneven heating of the catalyst particle, resulting in directed growth of nanowires in the lower, colder part.

EDS analysis showed that after thermal vacuum deposition, the catalyst particles consist of nonstoichiometric indium oxide. Apparently, the original indium particles are easily oxidized in air. At
the first stage of the synthesis, heating of the catalyst to operating temperature occurs in an oxygen atmosphere, so that the degree of oxidation of indium increases. Therefore, hydrogen plasma is necessary for the reduction of the particle to pure indium, which is in the liquid state at this synthesis temperature. This is evidenced by the spherical shape of the catalyst particles at the top of the microropes (Fig. 2a, b).

Figure 2. SEM image of silicon oxide nanostructures synthesized on indium catalyst particles of different average sizes: a) 42 nm, b) 79 nm, c) 170 nm, and d) 710 nm.

The difference in morphology between the microropes in Fig. 2a and 2b can be explained by the fact that for the catalyst with a smaller particle size, random factors have a more significant effect on the growth process, resulting in curved, feather-like, and thickened microropes. For the larger catalyst particles, these features disappear, and only well-oriented microropes are formed. For the catalyst with an average particle size of 170 nm, cocoon-like nanowire structures are formed. This morphology can be explained by the incomplete reduction of the catalyst particle to pure indium. Due to the large size of the catalyst particle, its lower part is not reduced by hydrogen plasma and remains solid. This leads to high supersaturation of the melt in the upper part, and nanowires grow isotropically. As a result, the particle is uniformly overgrown with silicon oxide nanowires. They block the access of silicon-containing radicals and the growth stops. With a further increase in the catalyst particle size to 710
nm, the hydrogen plasma reduces only a thin surface layer. As a result, nanowires are synthesized on a film of liquid indium. Apparently, the film breaks up into small catalyst particles on which microropes are formed. The SEM image shows that, as a result, a separate array of microropes is formed on each catalyst particle.

![Figure 3. Comparison of the morphology of nanostructures synthesized on indium catalyst particles with an average size of 710 nm (a) and on an ITO (b) film at a temperature of 200°C.](image)

An additional experiment was carried out to test the assumption that the synthesis of nanowires on very large catalyst particles proceeds in the same way as on a continuous catalyst film. The synthesis was carried out on an ITO film (material consisting of 90% In₂O₃ and 10% SnO₂) under the same conditions. Figure 3 compares SEM images for nanostructures synthesized on indium catalyst particles with an average size of 710 nm (a) and an ITO film (b). It can be seen that the morphology is similar in both cases: not very well-oriented microropes having approximately the same size and thickening with increasing length were formed. Thus, it is shown that, first, this method can be used to grow nanowires on an ITO film at a temperature of 200°C and, second, the synthesis of nanowires on catalyst particles of very large size proceeds in the same way as on the films. However, arrays of oriented microropes were not obtained.

![Figure 4. FTIR spectra of silicon oxide nanostructures synthesized on indium catalyst particles with different average sizes.](image)
The chemical composition of the synthesized nanostructures was determined from FTIR spectra (Fig. 4). The main features of the FTIR spectra are the Si–O asymmetric stretching mode (main peak) and the Si–O unsymmetric stretching mode (high-frequency shoulder). This indicates that the nanowires are composed of SiO\textsubscript{x}. According to [12], 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 SiO\textsubscript{x} material. The nanowires were found to consist of SiO\textsubscript{x} with x = 1.9. It has been previously shown [10] that if the ratio of the high-frequency shoulder to the main peak is greater than 0.5, arrays of microropes of nanowires are formed, and if this ratio is less than 0.5, a film or cocoon-like structures are formed. In the present study, this ratio is greater than 0.5 for all synthesized nanostructures, except for the structures grown on catalyst particles of 170 nm, which agrees with the results of the SEM analysis.

4. Conclusions

Silicon oxide nanowires were synthesized on an indium catalyst by gas-jet electron beam plasma-enhanced chemical deposition. The difference in morphology between the structures from nanowires grown on catalyst particles of different average sizes from 42 to 710 nm at 200°C was investigated. Microropes were synthesized on catalyst particles not larger than 80 nm. With an increase in the average size of catalyst particles to 170 nm, cocoon-like structures from nanowires were formed, and for 710 nm catalyst particles, the synthesis of microropes proceeded in the same way as on an ITO film. An indium catalyst with the particle size of 80 nm was found to be optimal for the formation of arrays of oriented microropes from nanowires. FTIR spectra were recorded to determine the chemical composition of the nanostructures. The nanowires were found to consist of SiO\textsubscript{x} with x = 1.9 assuming a uniform distribution of silicon and oxygen atoms.

In addition, EDS showed that the catalyst particles consist of nonstoichiometric indium oxide, rather than of pure indium. Therefore, for the synthesis of silicon oxide nanowires on indium catalyst, hydrogen should be used.

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