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Synthesis of indium nanostructure-laces by multi-step Glancing Angle Deposition

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HIGHLIGHTS

- Indium nanostructure-laces are synthesized by multi-step Glancing Angle Deposition.
- Each nanostructure-lace is composed of a nanowire-base trunk and uniform blocks.
- Indium blocks attach on In nanowires regularly.

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ABSTRACT

The synthesis of indium nanostructure-laces is achieved by multi-step Glancing Angle Deposition (GLAD). With combination of substrate rotation and air exposure in a multi-step deposition, we accomplished the uniformly assembling nanowires with nanoparticles. Analyses by transmission electron microscopy reveal the presence of pure indium composition. The growth mechanism of nanostructure-laces is studied and discussed. This result shows that multi-step GLAD is a simple and low-cost technique to fabricate nanostructures.

1. Introduction

Metal nanoparticles have exhibited great potentials in various applications, such as nanowires decoration [1], optical property research [2], optimizing assembly [3], etc. Due to the geometrical limitation, metal nanoparticles are often attached on organic/metal nanowires to construct hybrid nanodevices and 3D surface-enhanced Raman scattering (SERS) markers for excellent performance in many experiments [1,2]. The novel functionality other than original nanoparticles and nanowires makes these hybrid nanostructures attractive in potential applications of optoelectronic device fabrication and bio-sensing [3]. Self-assembly is the most common approach to decorate metal nanoparticles on nanowires up to date. Nonetheless, random coverage is often observed in hybrid nanostructures formed by self-assembly in solution. Although better properties may be obtained by regular decoration of nanoparticles on nanowires, controllable combination of metal nanoparticles and nanowires is still scarce in literatures.

Glancing Angle Deposition (GLAD) is usually reported as a one-step growth [4] method for one-dimensional metal nanomaterials. In the standard GLAD technique, in the process of physical vapor deposition, a substrate is tilted with respect to the evaporating flux direction, and one-dimensional nanostructures are formed on the inclined substrate due to the effect of adatom diffusion [5–8] and self-shadowing [4,9]. However, pure nanoparticle film is the result of most GLAD experiments and only several kinds of metal nanowires/nanowhiskers are prepared by one-step GLAD [7]. For example, low density of indium nanowires were deposited on normal silicon substrates by this method [9]. A development of the GLAD technique is the introduction of uneven Si substrates. Suzuki et al. reported that nanowhiskers of Al, Cu, Fe and other metals of high melting point could be prepared on patterned Si plates [5–7]. Reflection of evaporating flux from the trenched substrates was proposed as one extra reason for nanowhisker formation of various metals [5]. Up to date, all reports on the one-step growth show only one certain type of morphology, nanowire. It seems that the GLAD method cannot be used to produce complex nanostructures, for example, the integration or assembly of one-dimensional nanowires with nanoparticles in a controllable style.

Recently, we developed an improved technique, which we called multi-step GLAD, to fabricate indium nanostructure-laces.

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In addition to the large tilt angle of the substrate with respect to the evaporating flux direction, regular rotation of a sample holder and short time of air exposure were intentionally introduced in our GLAD experiments. This kind of novel nanostructures combines regular shaped nanoparticles on nanowires without any gap between them (shown in Fig. 1). This result shows that multi-step GLAD is a simple and low-cost technique to fabricate hybrid nanostructures by regularly combining nanoparticles and nanowires. One benefit of the multi-step GLAD method is the impurity of products, which should be less than that in the commonly-used self-assembly method because of the vacuum environment and the purity of the source materials. As an additional example of controllable assembly, we fabricate hybrid In–Sb nanostructures by this method. Our results show that GLAD is a method for regularly depositing metal nanoparticles on nanowires.

2. Experimental

We performed experiments in a vacuum depositing system (ULVAC VWR-400) with resistive heaters. The chamber was evacuated to about 3×10^{-3} Pa for deposition. Indium or antimony pellets (purity 99.99%) were used as the evaporation source. Si plates with SiO_2 top layer (thickness 300 nm) were used as the substrates. The substrate was fixed on a substrate holder which kept a distance of about 170 mm between the evaporation source and the substrate. In GLAD experiments, the tilt angle of the substrate inclined with respect to the vapor flux direction, defined as α could be adjusted from 0° to 90°, while $\alpha=85°$ was used in most cases to obtain the nanostructure-laces as confirmed in previous literatures [5–7,9]. The film thickness $d(\alpha)$ and deposition rate $\dot{d}(\alpha)$ for tilted substrates in GLAD can be calculated by two equations: $d(\alpha)=d_0\cos\alpha$ and $\dot{d}(\alpha)=\dot{d}_0\cos\alpha$, where d_0 and $\dot{d}_0$ represent the film thickness and deposition rate for normal deposition [5], respectively. d_0 and $\dot{d}_0$ were monitored by a quartz crystal oscillator in the vacuum chamber during the deposition process in our experiments. Normal deposition rate $\dot{d}_0$ from 0.5 to 10 nm/s ($\dot{d}(\alpha)$ from 0.04 to 0.87 nm/s) was tested in a series of experiments, and the rate of $\dot{d}_0=1$ nm/s ($\dot{d}(\alpha)=0.087$ nm/s) was found as an appropriate condition.

In our experiments, the deposition process was intentionally interrupted by several breaks. During the period of each break (usually longer than 10 min), the chamber was vented and the sample holder was rotated (usually in the angle of 90° or 180°). The actual motion of the substrate is, rotation around the axis of vapor flux, keeping the tilt angle of the substrate with respect to the vapor flux direction a constant ($\alpha=85°$). Two effects were generated after this procedure, the surface of samples would be naturally oxidized and the relative position between the substrate and the evaporation source was changed. Generally, a whole deposition process is composed of four or five discontinued deposition steps.

The morphology of the samples was observed by a scanning electron microscope (SEM, FEI Quanta 600). Highly magnified morphology, crystal structure and composition were analyzed by a high resolution transmission electron microscope (HR-TEM, FEI Tecnai F30) equipped with selected area electron diffraction (SAED) and energy dispersive X-ray spectroscopy (EDX).

3. Results and discussion

In normal single-step GLAD experiments, nanowires are grown usually at large glancing angle ($>80°$), which were described in previous literatures [4–7,9]. A similar situation (glancing angle $>80°$) was also found in our experiments to obtain nanostructure-laces. General morphology of the sample after multi-step GLAD is shown in Fig. 1. Bright and elongated nanostructure-laces are easy to distinguish from nanoparticles on the sample surface. The nanostructure-laces have length of several microns, and the longest one is close to 10 μm. Magnified details of these nanostructure-laces are shown in the inset of Fig. 1. We can see that each nanostructure-lace is composed of a nanowire-base trunk and some closely neighboring blocks. All blocks in one nanostructure-lace have similar shape and size. No gap between nanowire-base trunk and attached blocks indicates that the blocks are directly grown on the as-base nanowire, achieving the in-situ assembly of one-dimensional nanowires with nanoparticles. Nanostructure-laces of such kind are main products in our experiments, while a small amount of nanowires without assembly can also be found somewhere on the sample. We repeated this experiment for many times and nanostructure-laces appeared every time. Almost no morphology change was observed due to the change of deposition conditions, such as film thickness, deposition rate and substrate rotation angle.

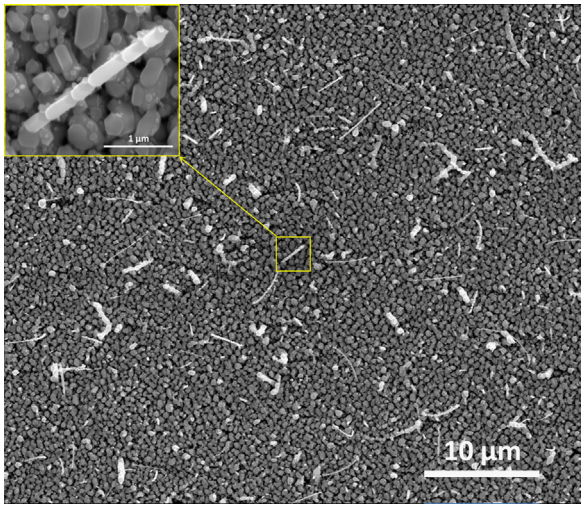

Fig. 1. SEM image of the sample morphology. Inset shows a highly magnified SEM image of one single nanostructure-lace.

The as-prepared nanostructure-laces are quite easy to transfer to other substrates, for example, the copper grid for TEM analysis. The composition of some nanostructure-laces was analyzed by EDX and a typical result is shown in Fig. 2(a). Indium is detected from the nanostructure-lace as expected, and strong Cu and C peaks are from the copper grid. A small amount of oxygen is probed from the sample, which may come from the oxidized surface of nanostructure-lace or the carbon film on the copper grid. This result reveals that pure In nanostructure-laces are formed in our GLAD experiments. Fig. 2(b) shows a bright-field TEM image of the tip of a nanostructure-lace. The smooth edges and regular shape of this block reveal a stable and continuous growth during the period of nanostructure-lace formation. The inset of Fig. 2(b) shows the selected area electron diffraction (SAED) pattern of this block. Most diffraction peaks can be indexed to a Tetragonal phase of In crystal (JCPDS 05-0642). Some thin white lines can be seen from the SAED image, which should be Kikuchi lines due to the large thickness of this block. A confusing question in SAED investigation is the origin of some redundant spots, such as the weak spot besides the (2 0 0) dot. It seems that there exist some small crystalline particles with a little changed lattice constant in the nanostructure-lace. Some irregular dark regions observed from the TEM image reveal the possibility of some defects, which will be analyzed in detail in the future. The crystal structure of nanostructure-laces was checked by HR-TEM and the micrograph of thin edge is shown in Fig. 2(c). The crystal fringes of [1 1 0] planes are marked in Fig. 2(c). It should be noted