Growth of Indium Nanorods by Magnetron Sputtering *

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Indium nanorods are grown on silicon substrates by using magnetron-sputtering technique. Film morphologies and nanorod microstructure are investigated by using scanning electron microscopy, high-resolution transmission electron microscopy (HRTEM), and x-ray diffraction. It is found that the mean diameter of the nanorods ranges from 30 nm to 100 nm and the height ranges from 30 nm to 200 nm. The HRTEM investigations show that the indium nanorods are single crystals and grow along the [100] axis. The nanorods grow from the facets near the surface undulation that is caused by compressive stress in the indium grains generated during grain coalescence process. For low melting point and high diffusivity metal, such as bismuth and indium, this spontaneous nanorod growth mechanism can be used to fabricate nanostructures.

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Recent years, one-dimensional (1D) materials, such as nanotubes, nanowires and nanorods, have been intensively investigated due to their novel properties (electrical, optical, magnetic, and mechanical properties) and their potential applications in nano-devices.[1] A variety of fabrication methods have been developed, including vapour–liquid–solid (VLS) growth,[2] template-based growth,[3] and oxide-assisted growth methods.[4] For lower melting point metal, such as Bi, compressive stress induced growth of nanowires was reported by Cheng *et al.*,[5] where the Bi nanowires were extruded by residual stress in composite films from the creak boundaries. Our previous work[6] on copper films grown by using magnetron sputtering also showed that the nanostructural hillocks or rods can be formed by residual compressive stress from grain boundaries, for example, triple junctions. In this Letter, we report the spontaneous growth of indium nanorods by the dc magnetron sputtering technique. We find that indium nanorod may easily be transformed into In_2O_3 nanorod by simple thermal oxidation. In_2O_3 is an important transparent conducting oxide material with a wide direct bandgap ($E_g \sim 3.6$ eV) and it has been widely used in solar cells[7] and gas detectors.[8] In_2O_3 in the nanorod form is expected to offer enhanced sensitivity for gas detectors. Apart from the above-mentioned applications, In_2O_3 nanostructures are also expected to be applied in field emission panel display.[9,10]

The experimental conditions are briefly summarized as follows. The sputtering power ranges from 5 W to 25 W. The chamber is filled with 99.999% Ar with the flowing rate of 10 sccm. The base pressure and working pressure are $\sim 5.0 \times 10^{-7}$ Torr and $\sim 2.5 \times 10^{-3}$ Torr, respectively. The target is an indium block of 99.99% purity. Before deposition the target is sputtered 10 min for cleaning. The substrate, which is about 4 cm away from the target, is a Si (100) wafer. Other substrates, such as glasses and carbon films, are also used. In all the cases, the substrates are cleaned ultrasonically in alcohol and then in acetone. The substrate is maintained at room temperature. The indium deposition rate (for 5 W and 25 W) ranges from 1 nm/s and 3 nm/s in our experiments. The films on different substrates are characterized using the scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and x-ray diffraction (XRD).

Figure 1 shows a high-resolution SEM image of indium film deposited on Si for about 10 min. It is clearly seen that the film surface is quite rough and covered with indium nanostructures, which have different shapes and sizes. Most of them are cylindrical nanorods and hemispheroidal nanostructures. We believe that the hemispheroidal nanostructures are the early growth stage of the cylindrical nanorods. The height of the nanorods ranges widely from 30 nm to 200 nm, and the diameter ranges from 30 nm to 100 nm. Films grown on glasses and carbon films show nearly the similar morphology, indicating that the growth of the indium nanorods is independent of the substrate material. Different sputtering pow-

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ers have also been used to grow indium films. It is found that the nanorods with an average diameter of $\sim$ 50 nm are always formed for sputtering power higher than 5 W. However, at lower sputtering power than 5 W, the nanorods uniformly distribute on the film surface with a lower density. The height of the nanorods is shorter than 50 nm, even if the deposition time is increased beyond 30 min. It should be mentioned that numbers of indium hillock formatting on film surface at this lower deposition power.[11]

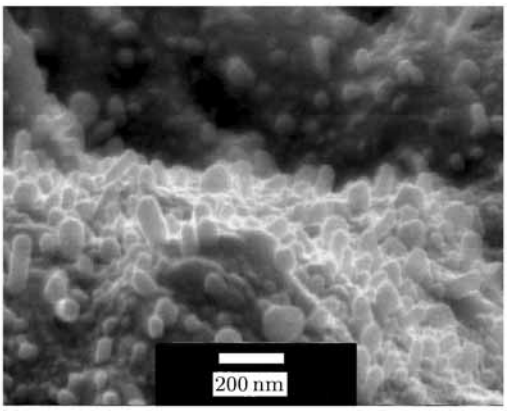


Fig. 1. Side-view SEM image of indium film deposited on Si (100) wafer for 10 min with sputtering power of 25 W.

To investigate the evolution processes of film morphology and nanorods, indium films with different thickness have been fabricated by controlling the deposition time. The SEM images of two typical snapshots are shown in Fig. 2. First, we note the evolution of film morphologies. For shorter deposition time (30 s in Fig. 2(a)), the film composed of large grains of hundreds nanometres in size has maze structure. The size of grains increases with the increasing deposition time. It is reasonable to believe that the grain coalescence plays a dominant role in the grain growing process.

It should be noted that numbers of nanodots (white spots) appear on the grain surfaces (Fig. 2(a)). The diameter of the nanodots ranges from 30 to 60 nm. The side view of SEM image (not shown here) shows that these nanodots are nanospheres or shorter nanorods. Compared Fig. 2(b) with Fig. 2(a), it is clear that both the density (number per unit area) and the size of the nanorods increase with increasing deposition time. The density increase implies that new nanorods grow from the grain surfaces. The side view of the SEM image for the film deposited for 6 min (Fig. 2(c)) shows that the height of the nanorods ranges from 30 nm to 170 nm and the diameter ranges from 30 nm to 90 nm. Compared Fig. 2(c) with Fig. 1, we find that the mean diameter and height of the nanorods increase slightly with increasing deposition time from 6 min to 10 min. The XRD results indicate that the crystalline structure of the deposited products is body-centred tetragonal indium (not shown here).

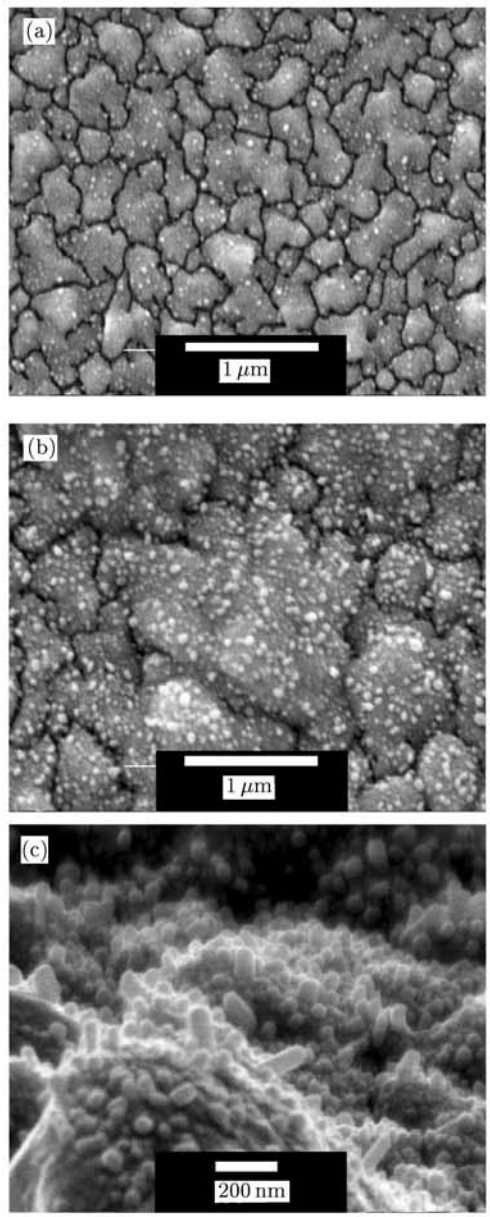


Fig. 2. Top- and side-view SEM images of indium film deposited on Si (100) wafer at 25 W for different deposition times: (a) 30 s, (b) 6 min, and (c) 6 min.

Figure 3(a) shows a TEM image for indium nanorods (side view), in which nanorods and nanospheres can be clearly seen. The sizes of these nanostructures are quite different. Selected area electron diffraction (SAED) patterns of nanorods reveal that they are single crystals. The inset SAED pattern taken from the nanorod marked by α can be indexed as the [001] pattern of a body-centred tetragonal indium phase. Figure 3(b) shows the HRTEM image of the middle part of the nanorod α. The distance between the lattice fringes is 0.322 nm, which is in

good agreement with the lattice plane spacing $\boldsymbol{d}$ (010) of body-centred tetragonal indium lattice with lattice parameters $a = b = 0.325$ nm and $c = 0.495$ nm. The [100] direction is parallel to the long axis of the

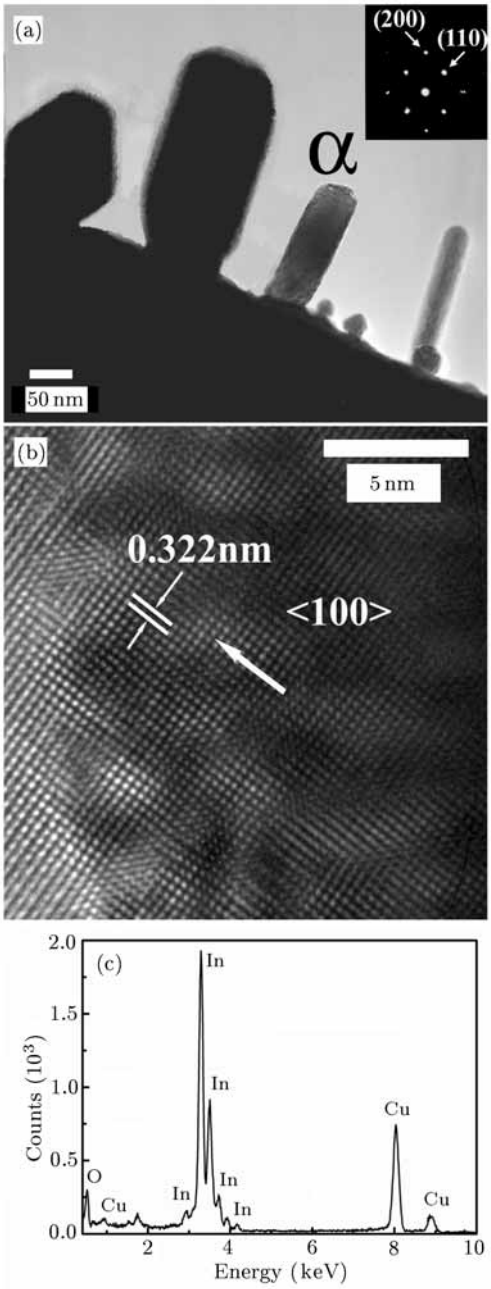


Fig. 3. (a) TEM image (side view) of the indium film deposited on Si (100) wafer at 25 W. The inset shows the select area electron beam diffraction (SAED) of grain α. (b) HRTEM image taken from a nanorod marked as α. (c) EDX spectrum obtained from the indium nanorods.

nanorod (arrow in Fig. 3(b)). This result indicates that the nanorod grows along the $\langle 100 \rangle$ directions; examination of more nanorods confirms this indication. To find the composition of nanorods, the energy-depressive x-ray spectroscopy (EDX) has been collected on the same nanorods. From the EDX spectrum, shown in Fig. 3(c), a small oxygen peak is seen. The oxygen may come from the very thin oxide layer on the nanorods, which is formed when the nanorods are exposed to air. The oxide layer should be very thin, because it cannot be detected from x-ray diffraction and electron diffraction results. The copper peaks in the EDX spectrum are due to the TEM copper grid.

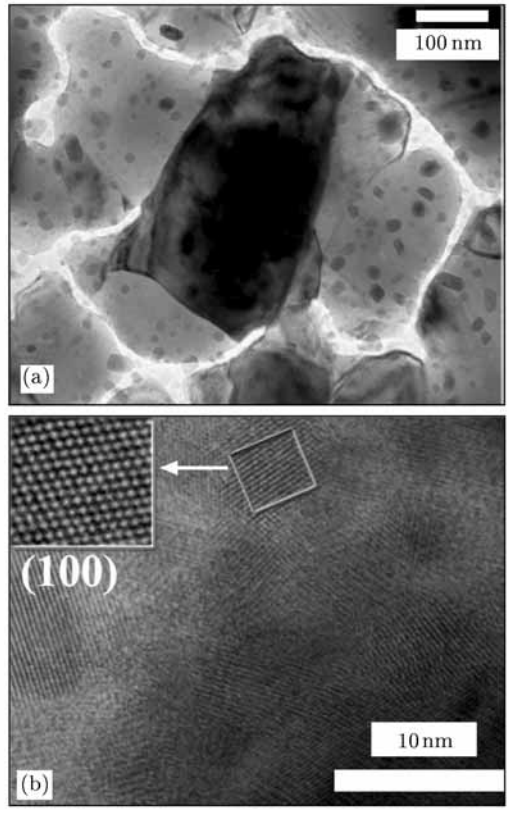


Fig. 4. HRTEM image (top view) of the indium film for different deposition times: (a) 2 min, (b) 30 s. Inset shows the HRTEM atomic image of one facet; clearly, it is a (100) facet.

Obviously, the growth mechanism for indium nanorods in this study is distinctly different from the nanorods in catalyst-assisted[2,3] and oxide-assisted growth,[4] and also different from the compressive stress induced Bi nanowires grown in the composite film.[5] It is evident in the SEM image (Fig. 2(b)) that almost all the indium nanorods grow from the grain surfaces not from grain boundaries. Screw dislocation, a possible mechanism for nanorod growth,[12] does not seem to work in our case, because no dislocations can be found at the positions where the nanorod grows up from the TEM images. Figure 4(a) shows a bright field TEM image of the indium film deposited on the carbon film coated on copper TEM grid. The indium grain boundaries, which are formed after smaller grain coalescence, are clear shown in this image. Numbers of nanorods (black dots) can be seen from this figure.

It is evident that almost no nanorods grow from the grain boundaries. Since no defects and dislocations are observed near the nanorods, the dislocation mechanism is not applicable to indium nanorod growth.

Although the detailed growth mechanisms for indium nanorods are not yet known, it is found from the HRTEM investigation that undulations do exist on the surface of the film deposited for 30 s, and there are many facets on the undulations surface. The HRTEM image (Fig. 4(b)) shows several facets. Inset is the HRTEM atomic image of one facet. Clearly, it is a (100) facet. The surface undulations are likely resulted from the compressive stress generated during the grain coalescence process at the early stage of the film growth. This compressive stress produced in grain coalescent process also provides a drive force for hillock growth at lower deposition power.[11] The stress deduced from the XRD measurements shows that the compressive stresses are about 210 MPa for the film of 200 nm in height deposited at sputtering power of 25 W. The surface undulations may release part of the stress in the films.[13] Therefore, it is suggested that the indium nanorods grow from the facets near the surface undulation caused by the compressive stress. The (100) facet provides an opportunity for the [100] nanorod growth. To confirm the speculation, the HRTEM observation has also been carried out for the films deposited with lower power ($P < 5$ W). Although some very short rods with much smaller density have been observed, the surface undulation is much weaker than that in the films deposited at high power. This is easily understood as follows. At very low power, both the adatoms and the small clusters have more time to migrate on the surface to release the elastic energy, which results much smaller stress.

In summary, indium nanorods have been grown on various substrates by dc magnetron sputtering at room temperature. The crystal structure, morphology and composition of the nanorods have been characterized by using a range of techniques. The single crystalline nanorods have the same body-centred tetragonal structure as the bulk indium. It is found from the HRTEM investigation that the rods grow along the [100] axis from the facets existing on the surface undulation. It is suggested that the compressive stress induced surface undulation may provide the growth condition for the nanorods. Of course, further work is needed to construct the whole picture of the growth mechanism of the indium nanorods.

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