ITO bi-crystal nanowires follow a grain boundary assistant growth mode

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In this work, indium tin oxide (ITO) bi-crystal nanowires (BCN), that coexist with the normal single crystal ITO nanowires, grown by the e-beam evaporation method are reported. The structure and the growth mechanism of the nanowire were studied by detailed high resolution transmission electron microscopy observations. Different to the conventional twin-structured nanowires that have a definitely defined crystal orientation relationship, ITO BCN were found to be composed of two single crystal nanowires welded with no definite orientation separated by a grain boundary. The detailed nucleation and growth processes of the bi-crystal nanowire were studied and a model based on the grain boundary assistant growth was proposed. It was realized that due to the presence of the grain boundary the two crystals were able to grow along some high indexed crystal directions. This mechanism plays the key role in the formation of special BCN structures.

Introduction

Nanowire materials have been found to have many novel applications in many fields due to their novel properties, such as enhanced optical emission, abnormal mechanical properties, and novel electrical characteristics. Most of their interesting physical and chemical properties are found to originate from their small size and the formation of different types of nanostructures, such as zig-zag nanowires, branched nanotrees, and helix nano-springs. It is recognized that the fabrication and growth mechanism study of new types of one dimensional (1D) nanostructures are central to their significance for application.

Many methods have been adopted to prepare special structured 1D nanostructures. For example, various solution-based processes were used to prepare different kinds of nanostructures in a controllable manner, such as the \( \alpha-CuV_2O_6 \) nanowires prepared using the hydrothermal method and the organic–inorganic coaxial nanowires prepared by the so-called coelectrodeposition method; chemical vapor deposition (CVD) is also a well developed method in 1D structure fabrication, such as the silicon carbide nanowires prepared by using the plasma enhanced CVD method (PECVD) following a well documented contact angle anisotropy model; other methods, such as in-plane growth with the aid of lithography and electric field induced growth of nanowires are also found to be novel methods in nanostructure preparation. It is seen that a lot of materials with various structural characteristics can be prepared by using different methods and good controllability can be achieved.

As a kind of special structure, twinned nanowires have been observed in many kinds of materials, such as ZnO, ZnS, ZnSe, GaP, SnO_2, and In_2O_3. Twin structures are featured as two mirror symmetrical crystals that share the same twin plane (parallel to the growth direction) with a dedicated orientation relationship, determined by the twin boundary energy, for given crystal structures. In contrast to the intensively studied twin nanowires, nanowires composed of two crystals with a non-dedicated orientation relationship (bi-crystal nanowire, brief as BCN below) have been rarely reported, although small/large angle grain boundaries are normally found in large sized 2-dimensional poly-crystal films or 3-dimensional ceramic bulk. As a matter of fact, due to the relatively larger grain boundary energy compared with the twin one, BCN with a grain boundary parallel to the growth direction, is relatively harder to grow in a 1-dimensional manner.

In this work, we report the observation of the bi-crystal ITO nanowires, which coexist with the normal single crystal ITO nanowires, prepared by an electron beam evaporation method without using any catalysis at low substrate temperature. Indium tin oxide (ITO) was studied because of its wide application in transistors light emission devices, solar cells and biology sensors, in which it was suggested that the formation of nanostructured ITO material is the key factor for enhancing the device performance. Although twin structured ITO nanowires were observed previously, the bi-crystal structured ITO nanowire was not observed. Here, we found the...
bi-crystal structured ITO nanowires have grain boundaries with various kinds of orientation relationship. The growth directions of the BCNs are not only limited in the normal low index planes.\textsuperscript{28–30} The detailed nucleation and the succeeding growth process were studied. A model based on the grain boundary assistant growth is concluded. It is found that the catalysing effect of the grain boundary has a very important effect on the formation of the bi-crystal structure. It is also anticipated that, due to the special nanoscale structure, the BCNs may show special mechanical, optical and electrical properties and may be used as components in advanced nanoscale devices.

Experiments

ITO nanowires were prepared using the e-beam evaporation method. ITO pellets (1–5 mm in size) with the atomic ratio of In/Sn = 95/5 were placed in a graphite crucible, used as source material. Carbon film sustained by copper mesh or aluminum foil was used as substrates for nanowire preparation, which was washed and dried overnight before use. The substrate temperature was fixed at 250 °C, which was controlled by a heater attached to the back of the sample holder. The growth process was monitored using a quartz crystal thickness controlling system. In order to achieve a precise control of the growth rate, the quartz crystal was assembled at the center of the sample holder near to the samples. Deposition of ITO nanostructures onto the substrate can be determined from the change of the thickness. A deposition velocity of around 2 nm s\textsuperscript{-1} was used for the growth of bi-crystal ITO nanowires. The base pressure before evaporation is normally around 2 × 10\textsuperscript{-4} Pa, and the working pressure during ITO deposition is around 1 × 10\textsuperscript{-2} Pa. More detailed information of the growth setup can be found elsewhere.\textsuperscript{8} The morphology and high resolution lattice image of the nanowires were obtained by using the transmission electron microscopy (TEM, Tecnai F20, or Tecnai G20). A low background Gatan double-tilt stage was used for studying the nanowire structure.

Results and discussions

Fig. 1(a) shows the TEM micrograph of the ITO nanowires after growth for about 20 minutes on aluminum foil. As seen in the figure, the nanowires have a diameter of around 30 nm and a length of about 200 nm. Most of the nanowires have an arrowed tip and uniform diameter. Two kinds of ITO nanowire can be found in the sample. One of which has the single crystal structure, as indicated by the hollow arrows in the figure. A typical high resolution TEM (HRTEM) image of the single crystal nanowire is shown in the inserted figure. The nanowire shows a body centered cubic (BCC) ITO with the growth direction of [100]. The lattice distance of 0.5 nm corresponds to the (100) planes, which accords well to our previous report.\textsuperscript{5} The other type of nanowire shows a totally different structure as indicated by the filled arrows. A HRTEM image of the nanowire was shown in Fig. 1(b). The nanowires were composed of two single crystal nanowires with a similar dimension growth along the same direction. Faced tip was also observed, which indicates the preferred growth of a specific crystal plane. At the tip of the bi-crystal nanowire, a notch is formed that separates the two single crystal nanowires from each other. Following our detailed tilting TEM observations, the two single crystal nanowires were found to be hemi-cylinder shaped with different crystal orientation that were welded by a grain boundary, as schematically shown in Fig. 1(c). The bi-crystal structure was modeled as two single crystal hemi-cylinder nanowires (SCHCs) welded at the grain boundary plane. They have a mirrored shape with respect to the central grain boundary plane. The notch formed at the tip between the two single crystal nanowires is just at the tip of the grain boundary. Elementary analysis using electron energy dispersive spectroscopy (EDS) shows roughly no evident

![Fig. 1](a) TEM image of the ITO nanowires with single crystal and bi-crystal morphology. HRTEM images of the ITO nanowire show single crystal (insert HRTEM image) and (b) bi-crystal structure. (c) Structure model of the bi-crystal nanowire composed of two SCHCs. It is noted also the project shape drawn by the shadow area with a dashed edge.
With a shorter growth duration, of the bi-crystal ITO nanowire, we prepared the ITO nanowires BCNs by our TEM observations. Orientation relationships were verified in more than 40 different (Fig. 2(d)), as indicated below the figures. The diverse was determined and the orientation relationships were found to be different: \(<01\bar{1}>_A \parallel <01\bar{2}>_B, (2\bar{1}1)_A \parallel (12\bar{1})_B\) (Fig. 2(a)); \(<01\bar{1}>_A \parallel <1\bar{3}5>_B, (2\bar{2}2)_A \parallel (12\bar{1})_B\) (Fig. 2(b)); \(<1\bar{2}1>_A \parallel <3\bar{1}2>_B, (10\bar{1})_A \parallel (2\bar{2}2)_B\) (Fig. 2(c)) and \(<2\bar{3}1>_A \parallel <01\bar{1}>_B, (2\bar{2}2)_A \parallel (2\bar{2}2)_B\) (Fig. 2(d)), as indicated below the figures. The diverse orientation relationships were verified in more than 40 different BCNs by our TEM observations.

In order to derive more information on the growth process of the bi-crystal ITO nanowire, we prepared the ITO nanowires with a shorter growth duration, i.e. 10 s and 25 s, onto carbon film (thickness \(\sim 2\) nm) sustained by copper mesh. Fig. 3(a)–(i) show the TEM results for the 10 s grown ITO nanostructures. As seen in Fig. 3(a) and (b), flat-lying winding nanostructures were observed on the substrate. They have diameters of 5–15 nm and lengths around 60 nm. Most of them were connected with each other. The formation of the winding nanowires could be due to the random condensation of the vapor flux on to the carbon film followed by lateral growth. Nanoparticles with diameters around 2–5 nm were also found on the substrate among the winding nanowires, as indicated in Fig. 3(e), which is the initial nucleus center for the winding nanowires. Fig. 3(c) shows the selected area electron diffraction (SAED) pattern of the nanowires. The diffraction rings from the \(\{110\}, \{002\}, \{112\}, \{004\}\) crystal planes were denoted in the ED pattern, which corresponds to the BCC structured ITO with a lattice parameter of 1.0 nm (JCPDF: 391058). The ring-shaped ED pattern indicates a random alignment of the winding nanowires. For each of the winding nanowires, a single crystal nature could be observed as shown in Fig. 3(d) and (f). The lattice spacing of 0.29 nm, 0.41 nm and 0.32 nm denoted in the figures corresponds to the \{222\}, \{211\} and \{310\} crystal planes of ITO, respectively. As no liquid catalysts were found, the vapor–solid (VS) condensation and succeeding 1D growth of the winding ITO nanostructure can be concluded.

A more important feature found in the 10 s grown sample is the formation of numerous spherical-shaped islands, as arrowed in Fig. 3(b). They have dimensions of 15–20 nm, and almost all of them are formed at the conjunction of the adjacent winding nanowires, in a head-to-head style (Fig. 3(g)–(i)) or side-to-side style (Fig. 3(f)). The islands were found to be composed by crystals with different orientations, which can be due to the randomly encounter of randomly distributed flat-lying nanowires during their in-plane growth. Observations found that the islands composed of four and three sub-crystals were very normal. Typically in Fig. 3(h) and (i), the islands are composed of three and two sub-crystals, respectively. Winding nanowires with different orientations connect to the island from different directions. The connected sub-crystals in the island have the same crystal orientations with the connecting flat-lying nanowires. In a word, due to the random growth directions and crystal orientation of the flat-lying nanowires, the island is formed randomly and uniformly on the substrate, composed of randomly oriented crystals. The islands composed of several sub-crystals were taken to be the nucleus of the BCNs.

With a longer growth period, distinct different features compared with the 10 s one were found. Fig. 4(a)–(d) shows the TEM results for samples grown for 25 s. More closely compacted structures can be seen in Fig. 4(a), indicating the continued growth of the nanostructures by the absorption of the incoming vapor species. The nanowires show diameters of around 20 nm and lengths of about 80 nm. From Fig. 3 and 4, the average growth rate of the nanowires can be calculated to be \(\sim 5\) nm s\(^{-1}\), which is evidently larger than the material deposition velocity. This indicates the (partial) transformation of the thin film growth to nanowire growth on the substrate. Also noted is that we did not observed very long nanowires in
samples with a long growth period, but only nanowires around several hundreds nanometer. This can be caused by the fact that part of the vapor species may condense among the nanowires, with a smaller growth velocity, and compete with the nanowire growth. Fig. 4(b) shows the TEM image of the bi-crystal nanowires. The grain boundary in the bi-crystal nanowires can be clearly resolved as indicated by the arrows. Single crystal nanowires were also seen to co-exist in the sample. Both the single crystal nanowires and the BCNs show similar dimensions, indicating a similar growth rate.

It is interesting that the islands formed by joining several nanowires in the 10 s grown sample (as discussed in Fig. 3(g)–(i)) were rarely observed in the 25 s one. Instead, most of the nanowires were found to have the bi-crystal structures. We thus infer that some growth directions in the previously observed islands should stop after a short growth period. The TEM images showing this situation are presented in Fig. 4(c) and (d). As shown in Fig. 4(c), the denoted nanowire is initially composed of three sub-crystals with different crystal orientations at the bottom, after a short growth, one of which dropped behind the other two, leaving a bi-crystal nanowire that keeps on growing. A similar process was also found in the transformation of a bi-crystal nanowire to a single-crystal nanowire. As seen in the Fig. 4(d), two nanowires with different crystal orientations were conjoined together at the lower part of the nanowire. The diameter of the attaching nanowire (the one with the smaller diameter) diminishes gradually from the bottom, while that of the other one remained unchanged. The previous one seized growth after a growth period, leaving the latter growth along the same direction. In both of the above examples, it is clearly seen that due to the competition growth of different crystal directions, the seized growth of the crystalline in the initial islands induces the transformation of the multi-junction nuclei to the bi-crystal or single crystal nanowires. These examples support our assumption.

As a competitive growth mode was observed, it is natural to ask the question: which growth mode is preferable during the growth process? We would like to interpret this based on the free energy related growth rates for different crystal planes. For

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**Fig. 3** TEM images of the 10 s grown ITO nanostructures with (a) low and (b) high magnification and (c) the corresponding SAED pattern. Green arrows indicate the junctions composed by more than two nanocrystals. Blue arrow indicates one single crystal nanocrystal. It also shows the HRTEM images of the crystal structure of (d) the winding nanowire, (e) small sized nanoparticles indicated by circles, (f) two winding nanowires attached to each other in a side-to-side fashion, and (g, h) the tri-junction and the (b) bi-junction. Arrows in (f)–(i) indicate the interface between the nanocrystals. Dashed lines with different colors indicate crystals with different crystal orientations in (g) and (i). Dashed red circle in (h) outlines the tri-junction.
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Eq. 1 shows the total free energy difference from vapor to solid, which means the growth rate is mainly affected by the surface energy, but near the grain boundary the total free energy is strongly related with the local curvature. (b) Model schematically shows the growth process of the bi-crystal nanowire: (i) nucleation of the flat lying ITO nanowire on the substrate, (ii)–(iv) extending in plane growth of the ITO nanowires until (v) they meet with each other and (vi) forms a junction, then (vii) the BCN which can grow from the junction follows the GAG mode.

For the bi-crystal or the multi-junction crystals, due to the existence of the grain boundaries, the growth rate will be determined by both the surface energy and an additional chemical potential caused by the curvature formed near the grain boundary. Following the Gibbs–Thomson equation: \( p/p_{eq} = \exp(-R_0/R) \), where \( R_0 \) is the critical nucleation radius and \( R \) is the curvature radius at the growth site of the surface, which means that the site with a smaller curvature radius will show a larger Gibbs free energy difference. So eqn (1) can be reduced as:

\[
\Delta G \sim k_1 \gamma + k_2 R^{-1}
\]

Where \( k_1 \) and \( k_3 \) are constant at a given temperature and pressure for a given material. It is shown that the free energy difference will be strongly influenced by the curvature radius especially when \( R \) tends to be small, for example at the tip of the nanowire. As a result, the site with a larger curvature will show a preferred growth tendency. In other words, for crystal planes with a lower surface energy, formation of the edges or notches will greatly increase their growth velocity.

The curvature related \( \Delta G \) at different sites around the tip of the bi-crystal nanowire was schematically shown in Fig. 5(a). In the multi-junction nanostructures, a notch with the curvature radius of only several nanometers is formed at the tip of the nanowire, just above the grain boundary, so in effect increasing \( \Delta G \) and the growth rate. Considering the crystal planes near the notch possess additional free energy caused by the curvature, the surface energy in different crystal planes
(k_{2}R^{-1}) will be potentially compensated by the free energy
induced by the curvature (k_{2}R^{-1}), the crystal planes should
be able to grow with priority and show a larger growth rate
than the crystal planes away from the notch. In the limiting
condition, the curvature radius tends to be very small, where
the Gibbs free energy could be much larger than the surface
growth, the growth rate may show little dependence on the
specific crystal planes and the crystal planes around the notch
will grow rapidly.

Except for the curvature structures formed above the grain
boundary, the grain boundary itself works as a low energy
nucleus site for vapor absorption. Due to the V-shaped notch
above the grain boundary, atoms absorbed at the grain
boundary edge/vapor triple phase interface have a higher
coordinate number, thus the free energy difference $\Delta G$
should be larger compared to separated smooth crystal surfaces.
Driven by the $\Delta G$, atoms may be absorbed directly from the
vapor or migrate from nearby crystal planes and contribute to
grain boundary growth with a higher probability.

As also shown in Fig. 4, grain boundaries were dragged
behind that transformed for the tri-crystal (bi-crystal) to bi-
crystal (single-crystal) structure. This was believed to be caused
due to the relatively fast growth rate of some crystal planes
compared with that of the grain boundary. Indeed, we did not
find a bi-crystal nanowire with any of its SCHCs growth along
the $<100>$ growth direction, while the $<100>$ growth
direction is only observed in single crystal nanowires (see
Fig. 1(a) insert). We thus infer that growth along other high
indexed directions may be more preferred under the current
growth mode. This also highlights the important effect of the
grain boundary in the formation of the bi-crystal structures.

It is also considered that if the growth along the grain
boundary is absent, i.e. only consider that the two crystals
aside the grain boundary grow according to the order of the
surface energy in different crystal planes, a “V” shaped
nanostructure will be probably more preferred to be formed
with each part growing along their $<100>$ directions. In this
case the bi-crystal structure will never form. On the other
hand, if only consider the continued growth around the grain
boundary, the notch at the tip of the nanowire will flatten
readily after a growth period, which will seize the further
growth along the grain boundary according to our previous
discussions. Considering these, we suggest that a coherent
mechanism involving two kinds of growth process, i.e.,
alternate growth of the grain boundary and the aside crystal
planes, may be able to make the two initially coupled nano-
crystals grown along the same direction in a continuous
manner. That is to say, a grain boundary assisted coherent
growth mode (GAG) plays the key role in the mechanism of the
BCN growth process.

Based on the GAG growth mechanism, the growth process
of the bi-crystal nanowires can be schematically illustrated in
Fig. 5(b). In the initial stage, the condenser of the vapor
species induced the nucleation of the ITO nanoparticles on to
the substrate. Subsequent growth of the nanoparticles follows
the substrate assistant lateral epitaxy, where the vapor species
prefer to condense to the contact line of the nanoparticle and
the substrate. With further growth, the nanowires contact
with each other in a random manner, the interface naturally
forming between them. Because the nanowire grows along
different crystal orientations, an interface with a random grain
orientation was formed. That is to say, two nanowires meet to
form bi-junctions, and three nanowires form the tri-junctions.
The multi-junctions served as the nuclei for the bi-crystal
growth. Following the GAG mode, the one dimensional growth
of the nanowire can be realized as a more energy favored
growth process. The transformation of the multi-junction
nanostructure to the bi-crystal or the single crystal nano-
structure is caused by the competitive growth process of
different crystal planes near the grain boundary. The crystal
planes with evidently slower growth rates lagged behind or
restrained gradually, leaving the grain boundary and other
crystals growing straight.

Summary
In this work, bi-crystal ITO nanowires with diameters around
30 nm were prepared using the e-beam evaporation method.
The crystal structure was studied and evaluated by TEM
observations. Bi-crystal structures with different orientation
relationships were found. The nucleation and the growth
process of the bi-crystal nanowires were evaluated. The
random nucleation caused by the meeting of adjacent
nanowires and the subsequent 1D growth is the initial step
in the formation of ITO bi-crystals. A growth velocity (along
the length direction) of $\sim 5$ nm s$^{-1}$ was found. The grain boundary
assistant growth process is the most important aspect in the
subsequent stable bi-crystal growth. The enhanced growth rate
driven by the free energy at the grain boundary by the
formation of notch structures is key for the grain boundary
assistant growth process. Due to the special crystal structure of
this BCN, we anticipate its special mechanical, optical and
electrical properties and also its use as components in
advanced nanoscale devices.

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References
1 S. Xu, Y. Qin, C. Xu, Y. Wei, R. Yang and Z. Wang, Self-


