Fabrication of nanocrystalline SnO$_2$ using electron stimulated oxidation

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Abstract
Fabrication of nanocrystalline SnO$_2$ using electron stimulated oxidation was investigated by in situ transmission electron microscopy. SnO$_2$ nanocrystals ranging from several to dozens of nanometers were transformed from single crystalline tin under 200 keV electron irradiation. This process includes crystallization of the surface amorphous SnO$_2$ layer and oxidation of the inner tin crystal substrate. On stimulation by electron irradiation, newly formed SnO$_2$ is supposed to act as a catalyst to oxidize the tin atoms underneath with lattice oxygen, and then be re-oxidized by absorbed oxygen from the residual gas of the microscope. This provides a new method to fabricate nanocrystalline SnO$_2$ materials and structures.

1. Introduction
Because of its special physical and chemical properties, SnO$_2$ has many important applications, such as solid state gas sensor, oxidation catalyst, as well as transparent conductor [1]. It has been reported that nanocrystalline SnO$_2$ possesses excellent properties during its applications [2, 3]. As a solid state gas sensor material, the crystallite size plays a key role in the sensitivity and response time of the gas sensor [4, 5]. When the crystallite size is comparable to the scale of the space-charge length (for SnO$_2$ the value is about 6 nm), the sensitivity of the nanocrystalline SnO$_2$ increases greatly as the crystallite size decreases.

There are many methods to fabricate nanocrystalline SnO$_2$ [6]. Leite et al [7] prepared SnO$_2$ nanoparticles through a special polymeric precursor method. Wang et al [8] proposed a solution-phase precursor route to prepare polycrystalline SnO$_2$ nanowires with nanocrystallites of about 5 nm in size, and the nanowires exhibited both high sensitivity and reversibility even under ambient conditions. Moreover, Nayral et al [6] synthesized nano-sized SnO$_2$ particles based on oxidation of tin nanoparticles. Furthermore, as we all know, electron irradiation can also stimulate the oxidation of metals [9, 10] as well as semiconductors [11, 12] that are exposed to oxygen atmosphere. Liu et al [13–15] reported the transformation of Fe$_3$O$_4$ from Fe$_3$N due to electron irradiation stimulated oxidation in a transmission electron microscope (TEM). This process can take advantage of electron beam lithography to control the position and size of the fabrication. Hence, it is necessary to explore this method to synthesize tin oxide from tin, which has never been investigated before.

Herein, we report the fabrication of nanocrystalline SnO$_2$ nanowires from the oxidation of tin whiskers with the stimulation of electron irradiation under high-vacuum conditions within a TEM, which suggests a new method to prepare SnO$_2$ nanomaterials on or within pure tin substrate.

2. Experimental procedures
The substrate used in this study was pure tin whisker, which grows from the rare-earth tin compounds (RESn$_3$) at room ambient conditions [16–18]. These tin whiskers are perfect single crystalline β-Sn without linear or planar defects. Their diameter varies from 20 nm to 10 µm, and those with diameter less than 50 nm are thin enough for high-resolution TEM (HRTEM) observations [19, 20].

Electron stimulated oxidation was carried out in a JEM-2100 microscope operated at 200 kV. The microscope runs with a column vacuum pressure in the range of 2–3 $\times$ 10$^{-5}$ Pa which is maintained with a sputtering ion pump. It has been concluded that the residual gases in the chamber of the TEM are mainly CH$_4$, CO, CO$_2$ and inert gases [21, 22]. Thus, the partial pressure of oxygen was estimated to be lower than 1 $\times$ 10$^{-6}$ Pa in our experiments. During the TEM observations, the normal electron beam size was about 300 nm in diameter,
and the beam current on the observation screen was around 88 PA cm$^{-2}$, which corresponds to 30.7 A cm$^{-2}$ on the specimen and a dose rate of about 1.98 × 10$^{24}$ e m$^{-2}$ s$^{-1}$ for electron irradiation. In order to observe the initial stage of the specimen, a tin whisker in low index orientation was selected as quickly as possible to record the bright field (BF) images and electron diffraction pattern (EDP), which was defined as the starting point of the irradiation. Moreover, HRTEM images were also recorded during the in situ observation with increase of the electron irradiation time at room temperature.

3. Results

3.1. Conventional TEM investigation

Figure 1 shows a series of BF images and the corresponding EDPs of two tin nanowhiskers subjected to irradiation of 200 keV electrons at different stages. Whisker A is small and short like a tip, as shown in figure 1(a), while whisker B has a trunk of about 50 nm in diameter. The fresh whisker has a smooth surface layer with light contrast, which is considered as an amorphous tin dioxide layer around the whisker body [17, 23]. It is noteworthy that these two whiskers grew with the same crystal orientation. Both of them show the EDP of $\beta$-Sn in the [111] axis, as illustrated in figure 1(b). Moreover, since the whiskers endured slight electron irradiation during the beam adjustment and specimen tilting, a small part of the amorphous layer over the whisker had transformed into nanocrystals, and the newly formed nanocrystals show some extra spots in the electron diffraction, as indicated by the arrowheads in figure 1(b). After 19 min of irradiation, as shown in figure 1(c), many nano-size black clusters covered the whisker surface. Meanwhile, the whisker matrix became thinner, and the surface became rather rough compared with its initial stage in figure 1(a). Correspondingly, the EDP of the two whiskers shows a series of additional diffraction rings, as indicated by the arrowheads in figure 1(d), which cannot be indexed with solid evidence because of the limited information. Although diffraction spots from the original tin [111] still exist in figure 1(d), they are not in perfect symmetry any more due to the slight tilting of the whisker under electron irradiation. When the two whiskers endured electron irradiation for 54 min, as shown in figure 1(e), the black clusters has encroached on the whole body of the whiskers. The corresponding EDP is shown in figure 1(f), which is made up of serial diffraction rings. This implies that the thin parts of the tin whiskers have totally transformed into nanocrystalline material, and the interfaces are indicated by the dotted lines. To identify the newly formed nanocrystals, tin related oxides were used to index the diffraction rings in figure 1(f), because it has been reported that the residual oxygen in the high-vacuum of a TEM is still active enough to electron sensitive material under electron irradiation [13]. After careful examination, these nanocrystals were identified as rutile SnO$_2$ (PDF Card 77-0451), and their top 10 standard diffraction rings were drawn artificially in figure 1(g), showing good coincidence with the experimental results in figure 1(f). This was also verified by HRTEM observations, which will be discussed later. Herein, it is concluded that the original tin whiskers endured oxidation and transformed into nanocrystalline SnO$_2$ whiskers with the stimulation of electron irradiation in the high-vacuum of the TEM.

3.2. High-resolution TEM observation

The detailed oxidation process was also investigated by in situ HRTEM observations. Firstly, it was found that crystallization of the surface amorphous layer took place on the tin whiskers. At the initial stage, there was a layer of amorphous tin dioxide all over the tin whisker body [17, 23]. When the whisker was subjected to electron irradiation, the surface amorphous tin oxide transformed into crystalline SnO$_2$ gradually. Figure 2 shows this process viewed along the [010] zone axis of a tin whisker. The surface amorphous layer on the tin whisker body is manifested in the original HRTEM image of figure 2(a), which exhibits uniform light contrast. After electron irradiation for 4 min, as shown in figure 2(b), the right part of the surface amorphous oxide turned into crystalline SnO$_2$, while the left part was still in an amorphous state (the interface is indicated by a dotted line). Furthermore, at the interface between the tin matrix and the SnO$_2$, there are many lattice steps on the (020) plane along the [010] direction, as indicated by the arrowheads in figure 2(b). These lattice steps are directly related to defects like vacancies and interstitial atoms, which could contribute to the oxidation of tin in the following stage.

Secondly, the crystallized surface SnO$_2$ layer still grew thicker as the electron irradiation progressed, and the inner pure tin was consumed gradually. Finally, the thin part of the tin whisker could transform completely into SnO$_2$ nanowire. Figure 3 shows a series of HRTEM images of whisker A in the area indicated by the dashed rectangle in figure 1(c). Figure 3(a) is an image of the whisker at the set starting point of the irradiation. The whisker has experienced electron irradiation somewhat during the image adjustment, hence part of the original amorphous surface oxide exhibits the characteristics of crystal, as indicated by the arrowheads. Therefore, the EDP of whisker B in figure 1(b) shows extra spots besides the [111] of $\beta$-Sn, as indicated by the arrowhead. Figure 3(b) was recorded 6 min later; here, the surface amorphous oxide has transformed totally into crystalline SnO$_2$ on the outside of the whisker. The SnO$_2$ layer began to encroach on the tin whisker as the tin body became thinner compared with its original state in figure 3(a). The whisker became even thinner after electron irradiation for 27 min, as shown in figure 3(c), and the morphology of SnO$_2$ nanocrystals can be seen clearly. Furthermore, the whisker underwent great change in the next 32 min, as depicted clearly in figure 3(d), which shows that the tin matrix was completely encroached by SnO$_2$ grains, and the original tin whisker transformed completely into SnO$_2$ nanowire. The in situ growth of a SnO$_2$ nanocrystal is outlined with dotted lines in figure 3 to illustrate its morphological development with the prolonging of irradiation time. It originated within the surface amorphous layer with a diameter of about 5 nm...
Figure 1. Bright field images of tin whiskers exposed to electron irradiation for (a) 0 min, (c) 19 min and (e) 54 min; the corresponding EDPs are shown in (b), (d) and (f), respectively. (g) The standard diffraction rings of rutile SnO\textsubscript{2} calculated from PDF Card 77-0451. The series diffraction patterns were obtained from the areas illustrated by the dashed rings, the diameter of which is about 110 nm, during \textit{in situ} investigations.

at its initial forming stage (figure 3(a)), and grew to about 9.5 nm by consuming nearby amorphous atoms under the stimulation of the electron irradiation after 6 min (figure 3(b)). Then, the crystallite started to consume the inner/underneath tin matrix to grow even larger, to about 10.5 nm after 27 min (figure 3(c)). Finally, this SnO\textsubscript{2} crystallite grew to about 12 nm in diameter when the tin whisker body was consumed completely, and SnO\textsubscript{2} nanowire was formed. This kind of SnO\textsubscript{2} nanowire consists of nanocrystals with an average grain size of about 7 nm, and the grain boundaries of neighboring crystals are clearly seen, as indicated by the arrowheads in figure 3(d). The atomic arrangement and planar spacings of the crystal’s HRTEM image in figure 3 agree very well with those of rutile SnO\textsubscript{2}, which also verifies the phase identification according to the EDP in figure 1.

4. Discussion

4.1. Crystallization of the surface amorphous SnO\textsubscript{2} layer

There is an oxide layer on the surface of the tin whiskers, which is amorphous SnO\textsubscript{2} at room ambient conditions. According to \textit{in situ} TEM observations, this amorphous tin oxide layer gradually transformed into crystalline SnO\textsubscript{2} when the whiskers were subjected to electron irradiation. It has been reported that electron irradiation can stimulate crystallization...
Figure 2. HRTEM images of a whisker subjected to electron irradiation for (a) 0 min and (b) 4 min. The interfacial steps on the (020) plane are indicated by the arrowheads in (b).

of amorphous materials [24, 25]. Thus, we believe that the disordered Sn and O atoms in the amorphous SnO$_2$ would reconstruct due to the activation of the 200 keV electron irradiation to form ordered crystalline SnO$_2$. Stimulated by high energy electrons, nuclei can form easily all over the surface amorphous oxide layer, so the crystal size of the SnO$_2$ formed is in the range of only several nanometers. As a whole, the crystallization of the surface amorphous layer can be described as

$$\text{Sn}_{\text{amorphous}} + 2\text{O}_{\text{amorphous}} \xrightarrow{\text{electron irradiation}} \text{SnO}_2(\text{crystalline})$$

4.2. Oxidation of pure tin by the self-catalyzed process

After the surface amorphous SnO$_2$ has transformed into SnO$_2$ crystals, the nanocrystalline SnO$_2$ layer covers the whole tin whisker body. As this amorphous crystallization process under electron irradiation is not an equilibrium one, there are many defects like lattice vacancies in the nanocrystalline SnO$_2$, and the newly formed surface nanocrystalline SnO$_2$ layer can act as a catalyst to oxidize the inner tin matrix during the following electron irradiation. It has been reported that natural non-stoichiometric SnO$_2$ is an oxidation catalyst in its own right [1, 26], and its mechanism is supposed to follow the Mars–van Krevelen mechanism [26], like most other metal oxide catalysts [1], under which the metal atoms are oxidized by consuming lattice oxygen of the metal oxide catalyst which in turn is re-oxidized by outer oxygen. This is possible for SnO$_2$ during stimulated oxidation of tin because tin has multivalent oxidation states that allow SnO$_2$ to easily give up lattice oxygen and then subsequently be re-oxidized further. The oxidation of the tin whisker at the interface between the crystalline SnO$_2$ and the tin matrix stimulated by electron irradiation is supposed to be as follows.

Figure 3. HRTEM images showing the in situ oxidation process after electron irradiation for (a) 0 min, (b) 6 min, (c) 27 min and (d) 59 min. The growth of a SnO$_2$ crystal is outlined.
With the stimulation of the 200 keV high energy electrons, the surface tin atomic bonding is broken; hence, tin atoms escape from the whisker body, and at the same time the non-stoichiometric SnO$_2$ nanocrystals give up lattice oxygen which react with the released tin atoms to form SnO$_2$ by formula (2). In this reaction, the role of electron irradiation is to accelerate the breaking of the atomic bonding of pure tin to provide released tin atoms, and hence to improve the oxidation rate, because it is known that the oxidation of pure tin is very slow at room ambient conditions without an electron beam. It is noteworthy that four electrons are released according to formula (2). These released electrons are injected into the SnO$_2$ layer, which is essential for the next step of the re-oxidation,

\[
2O^{2-}_{\text{lattice}} + \text{Sn} \xrightarrow{\text{electron irradiation}} \text{SnO}_2 + 4e. \tag{2}
\]

The re-oxidation of SnO$_2$ is a rather complicated process including different electron–solid reactions and charge transportation. Firstly, the electron beam will enhance the adsorption of oxygen on the surface of the crystalline SnO$_2$ layer. Typically, when non-stoichiometric SnO$_2$ is exposed to oxygen environment, oxygen gas is adsorbed on the surface of the SnO$_2$. It is the same for the residual oxygen in high-vacuum conditions, and the adsorption is accelerated by the stimulation of electron irradiation. Once the oxygen species is adsorbed onto the surface SnO$_2$, it will capture electrons (see formula (2)) from the inner SnO$_2$ crystals, and turn into mainly molecular O$_2$ at room temperature [27]. Secondly, the molecular O$_2$ will transform into O$^-$ by capturing further electrons released from the reaction of formula (2) under electron irradiation, since molecular O$_2$ is electrophilic and the transformation can reduce the relative energy. Thirdly, with the stimulation of high energy electron irradiation, the electrophilic O$^-$ transforms into unstable O$^{2-}$ on the surface. This process is very difficult to achieve at room temperature without electron beam irradiation, since O$^{2-}$ has much higher relative energy than O$^-$ species [27]. Finally, since the formation energy of oxygen vacancies in non-stoichiometric SnO$_2$ is very low according to Kılıç and Zunger’s study [28], oxygen vacancies in non-stoichiometric SnO$_2$ can form readily due to the multivalence of tin. Therefore, the unstable O$^{2-}$ occupies a lattice oxygen vacancy immediately and becomes lattice O$^{2-}$ to reduce the non-stoichiometric SnO$_2$.

The re-oxidation of the nanocrystalline SnO$_2$ described above can be summarized with the following formulas in which the electron irradiation stimulates adsorption of oxygen and the formation of O$^{2-}$ species on the surface:

\[
\begin{align*}
\text{O}_2 + e \xrightarrow{\text{electron irradiation}} & \text{O}_2^- \tag{3} \\
\text{O}_2^- + e \xrightarrow{\text{electron irradiation}} & \text{2O}^- \tag{4} \\
\text{O}^- + e \xrightarrow{\text{electron irradiation}} & \text{O}^{2-}_{\text{surface}} \tag{5} \\
\text{O}^{2-}_{\text{surface}} \xrightarrow{\text{oxygen vacancy}} & \text{O}^{2-}_{\text{lattice}} \tag{6}
\end{align*}
\]

The two tin whiskers used to fabricate SnO$_2$ in the experiment grew on the nearby tin matrix, and the whisker samples can be regarded as traditional TEM specimens since the irradiation area was near the edge of the tin matrix. Concerning the heating effect of the electron beam during the TEM observations, it has been reported that for a typical Al–1.5 wt% Mg specimen, the average local rise in temperature is approximately 6°C under typical normal working conditions [29]. In addition, beam heating for thin metal specimens is negligible under standard TEM conditions and generally it can be minimized by reducing the cross section for inelastic scattering according to [30]. Since the tin whisker used in this experiment was very thin (less than 60 nm, as shown in the BF images, which is of the same order as the mean free path of tin at 200 kV [30]) and tin metal is a good thermal conductor, the local rise in temperature should be very small.

Furthermore, Liu and Risbud [31] developed a method to evaluate the temperature rise in Al–Si particles embedded in a thin film. Yokota et al [32] modified this method to evaluate the temperature rise in the Al–Si particles. The temperature rise can be estimated as

\[
\Delta T \approx \frac{3JQ}{8efdR^2 \ln(1 + \frac{4k_1t}{fdR^2})}, \tag{7}
\]

where $J$ is the electron beam current density, $R$ is the radius of the particle, $f$ is the specific heat, $d$ is the mass density, $k_1$ is the thermal conductivity, $t$ is the irradiation time and $Q$ is the total energy loss of the electron.

The temperature rise of the tin whisker was calculated according to formula (7), assuming that $R$ is the radius of the whisker and the whisker is pure tin, using $J = 30.7 \times 10^4$ A m$^{-2}$, $R = 60 \times 10^{-9}$ m, $f = 2.27 \times 10^3$ J kg$^{-1}$ K$^{-1}$, $d = 7.30 \times 10^3$ kg m$^{-3}$, $k_1 = 66.6$ J m$^{-1}$ s$^{-1}$ K$^{-1}$, $t = 3.6 \times 10^3$ s. $Q$ and its related parameters are given in [32]. The temperature rise of the tin whisker at 200 kV was calculated to be less than 1°C in our experiments. Thus, the heating effect of electron beam irradiation on thin tin whiskers can be neglected in this study.

4.3. Fabrication of nanocrystalline SnO$_2$ using electron beam lithography

Therefore, transformation from pure tin to nanocrystalline SnO$_2$ was achieved by electron stimulated oxidation. This process includes crystallization of the surface amorphous tin oxide layer (formula (1)), oxidation of the inner tin by crystallized SnO$_2$ as a catalyst (formula (2)), as well as re-oxidation of the non-stoichiometric SnO$_2$ catalyst (formulas (3)–(6)). Using this technique, SnO$_2$ wrapped tin nanowire can also be fabricated artificially. Figure 4(a) shows two tin nanowires of about 50 nm in diameter, which are wrapped with a layer of nanocrystalline SnO$_2$. After being subjected to uniform irradiation, nanowire C has a uniform SnO$_2$ layer that is about 5 nm in thickness on both sides. However, nanowire D shows a nonuniform SnO$_2$ layer on the surface, which is about 20 nm on the left side but only about 5 nm on the right side. Figure 4(b) is the HRTEM image...
of the crystallized SnO$_2$ layer (~5 nm) on the right side of nanowire D. This asymmetric microstructure was achieved by using different irradiation time on the two sides of nanowire D.

Besides SnO$_2$ nanowires and SnO$_2$ wrapped tin nanowires, different microstructures of SnO$_2$ could be fabricated on tin particle, film and bulk materials. By using the flexibility of electron beam control [33, 34], nanocrystalline SnO$_2$ could be fabricated at any local position with various shapes on tin film substrate, which extends the application potential of electron beam lithography. It is necessary to point out that due to the current limitations of electron beam generation, this technique only provides small areas of nanocrystalline SnO$_2$ with the merit of controlled fabrication on the nanometer scale, but is still a long way from wide application in the catalysis industry. With the development of electron irradiation systems, this technique is expected to be more flexible in the near future.

5. Conclusions

The fabrication of nanocrystalline SnO$_2$ with pure tin using electron stimulated oxidation was investigated by in situ TEM. Stimulated by 200 keV electrons at a dose rate of about $1.98 \times 10^{24}$ e m$^{-2}$ s$^{-1}$, the residual gas in the vacuum of 2–3 $\times 10^{-5}$ Pa is still active enough to oxidize tin atoms to form SnO$_2$ nanocrystals with an average diameter of around 7 nm. Owing to the electron beam irradiation, the intrinsic surface amorphous SnO$_2$ on the pure tin reconstructed into SnO$_2$ crystals first, and then this crystallized SnO$_2$ acted as a catalyst to oxidize and consume the tin matrix. The stimulated oxidation of tin is supposed to be a self-catalyzed process following the Mars–van Krevelen mechanism, which includes oxidation of the tin atoms by the lattice oxygen of SnO$_2$ and re-oxidation of the SnO$_2$ by adsorbed oxygen species. This technology can be used to fabricate different kinds of SnO$_2$ nanomaterials and structures with pure tin.

Acknowledgments

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References

[18] Li C F, Liu Z Q and Shang J-K 2013 The effects of temperature and humidity on the growth of tin whisker and hillock from Sn₅Nd alloy J. Alloys Compounds 550 231–8
[33] Liu Z Q, Mitsuishi K and Furuya K 2004 Effects of focus change on the fabrication of tungsten nanowire by electron-beam-induced deposition Nanotechnology 15 S414–9
[34] Zhang W, Liu Z Q and Furuya K 2008 Fabrication and characterization of cellular iron nanocrystalline film Nanotechnology 19 135302