Temperature-dependent growth mechanism and microstructure of ZnO nanostructures grown from the thermal oxidation of zinc

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A R T I C L E  I N F O
Article history:
Received 26 September 2013
Received in revised form 12 December 2013
Communicated by A. Ohtomo
Available online 28 December 2013

Keywords:
A1. Crystal morphology
A1: Characterization
B1. Nanomaterials
B1. Zinc compounds
B1. oxides

A B S T R A C T
We report a detailed study on the growth morphologies and microstructure of ZnO nanostructures formed from the oxidation of Zn at different temperatures. ZnO shows bicrystalline nanowire morphology for oxidation below the melting point of Zn, and single-crystalline morphology between the melting and boiling points of Zn, and tetrapod morphology above the boiling point of Zn. The morphological and microstructural variations are attributed to the temperature-dependent oxide growth mechanisms, i.e., the oxidation below the melting point of Zn is dominated by a solid–solid transformation process, a liquid–solid process between the melting and boiling points of Zn, and a vapor–solid process above the boiling point of Zn. The understanding of the oxide growth mechanisms from these results may have practical implications for rational control of the morphology, crystallinity, preferential growth directions, shape and aspect ratio of ZnO nanostructures.

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1. Introduction
Zinc oxide (ZnO) is a direct wide-bandgap semiconductor (3.37 eV) with large exciton binding energy (60 meV). ZnO has received intensive interest for its unique properties and wide applications in optics, optoelectronics, sensors, biomedical sciences actuators, energy, and spintronics [1–3]. Shrinking its size to the nanoscale is expected to open an even wider range of technical possibilities such as nanophotonics, nanoelectronics, and nanobiotechnology [4,5]. ZnO nanostructures with diverse morphologies have been produced, including wires [6,7], belts [8], tubes [9], rods [10], springs [11], rings [12], sheets [13], and tetrapods [14–16]. The approaches used for growing ZnO nanostructures mainly include vapor–solid [17–19], vapor–liquid–solid [20], epitaxial growth [21,22], hydrothermal [23], and solution processes [24]. More recently, thermal oxidation of Zn has been used to grow ZnO nanostructures [25–31]. Compared to the catalyst-assisted growth, direct oxidation of metallic zinc is a simple, cost effective and non-catalytic approach for producing ZnO nanostructures with large-scale growth capabilities and high purity owning to the elimination of intermediaries involved in catalytic chemical synthesis of oxide nanostructures.

Directly heating Zn foils or powders under oxygen gas flow results in the formation of various ZnO nanostructures with a large variety of morphologies [26,32,33]. Due to its capabilities of producing a rich variety of morphologies of nanostructures, the vapor–solid mechanism is usually invoked to understand the oxidation-induced ZnO nanostructure growth, in which Zn evaporates from the raw material and reacts with gaseous oxygen to form nanostructured ZnO [26,32,33]. The temperatures reported for ZnO nanostructure formation during oxidation vary typically from 400 to 1000 °C, which cover the melting temperature (420 °C) and boiling temperature (907 °C) of Zn. While Zn has a relatively high vapor pressure at these oxidation temperatures, particularly above the boiling temperature, the rapid oxidation of Zn to form a solid ZnO coating layer on the Zn substrate surface can effectively prevent further Zn evaporation from the Zn substrate. Meanwhile, decomposition of ZnO requires a temperature up to ~1400 °C [34], which is much higher than the oxidation temperatures (i.e., 400–1000 °C) typically employed for ZnO nanostructure growth. This implies that the growth of ZnO nanostructures should stop quickly soon after the formation of a solid ZnO coating layer on the Zn substrate, but this is actually not the case since many experimental results have demonstrated that a longer oxidation time results in the formation of more ZnO nanostructures on the Zn surface [35]. Such controversies suggest that the vapor–solid process may not be the only mechanism responsible for ZnO nanostructure formation during the oxidation of Zn. A detailed and clear understanding of the growth
mechanisms is essential for rational control of the morphology, crystallinity, preferential growth directions, shape and aspect ratio in an efficient way.

Motivated by the aforementioned questions and speculations, we perform a systematic study to ascertain the morphological and microstructure evolution of ZnO nanostructures during the oxidation of Zn substrates. Particularly, we examine the effect of oxidation temperature on ZnO nanostructure formation. Indeed, we find that the mechanism governing the formation of ZnO nanostructures actually depends on the oxidation temperature. At the oxidation temperature below the melting of Zn, the formation of ZnO nanostructures occurs via a solid–solid transformation mechanism, in which the relaxation of the compressive stresses generated by the volume mismatch accompanying the ZnO/Zn interfacial reaction stimulates the formation of bicrystalline ZnO nanowires. For oxidation at the temperature above the boiling point of Zn, ZnO nanostructures occur via the vapor–solid mechanism, in which Zn evaporates from the Zn substrate and reacts with gaseous oxygen to form solid ZnO that precipitates onto the surrounding areas. For oxidation at temperatures between the melting and boiling points of Zn, the liquid–solid mechanism is the dominating process that results in the formation of single crystalline ZnO nanowires on the Zn substrate.

2. Experimental details

High-purity Zn foils (99.99%) with a thickness of 0.25 mm obtained from Sigma-Aldrich are used in the oxidation experiments. Gold (10 nm) coated Si(111) wafers serve as the deposition substrates that are placed next to the Zn foils. A chromium primer layer (~2 nm) is coated before Au coating to improve adhesion between the gold layer and the silicon substrate. The oxidation experiments are carried out in a horizontal tube furnace. The silicon substrates next to the Zn foil is to examine if there is any ZnO formation mechanism in the dominating process that results in the formation of ZnO nanowires on the Zn substrate.

Fig. 1. Schematic illustration of the experimental setup for the oxidation of Zn.
then deposited onto the surrounding area including the Si surface. Increasing oxidation temperature results in more Zn evaporated from the Zn foil and therefore more ZnO deposited on the Si surface. This can also be evidenced by measuring the thickness of the Zn foils oxidized at the different temperatures. As shown in Fig. 4, the thickness of the oxidized Zn foils first increases with increasing the oxidation temperature, and then starts to decrease for oxidation at the temperatures above the melting point. The Pilling–Bedworth ratio (PBR), \( \text{PBR} = \frac{\text{volume of formed oxide}}{\text{volume of consumed metal}} \), is 1.58 for ZnO formation from the oxidation of Zn, i.e., the volume of the oxide formed is larger than that of the metal consumed. Therefore, for oxidation below the melting point of Zn, the oxide is directly formed on the Zn substrate, which results in the increased total thickness of the oxidized Zn foil. For oxidation above the melting point of Zn, some of the Zn is evaporated from melted Zn to form ZnO powder which is taken away by the gas flow, therefore, the total thickness of the oxidized Zn foil becomes thinner (note that the oxidation at 1000 °C results in complete evaporation of the original Zn foil in the ceramic boat).

Fig. 2. Representative SEM images of the Zn surfaces oxidized at different temperatures: (a) 200 °C, (b) 300 °C, (c) 400 °C, (d) 500 °C, (e) 600 °C, and (f) 800 °C.

Fig. 3. SEM images of the Si substrates placed next to the Zn foils oxidized at (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C, (e) 800 °C, and (f) 1000 °C.

Fig. 4. Dependence of the sample thickness (including the Zn substrate and the ZnO layer formed from the oxidation) on oxidation temperature. Note that the original thickness of the Zn foils before being subjected to oxidation is 0.25 mm.
It becomes evident from the above observations that the ZnO formation occurs via three different mechanisms, depending on the oxidation temperature. For oxidation at the temperatures below the melting point of Zn, the oxide forms via a solid–solid transformation resulting in the growth of a ZnO overlayer on the Zn substrate with formation of ZnO nanowires on the ZnO overlayer. For oxidation at the temperature above the boiling point of Zn, ZnO formation occurs via the vapor–solid transformation in which Zn evaporates from the Zn foil and reacts with oxygen to form ZnO tetrapods which are deposited onto the surrounding area (including the Si wafer). For oxidation at the temperatures between the melting and boiling points of Zn, two mechanisms operate simultaneously for ZnO formation. One is the liquid–solid mechanism that results in the growth of ZnO nanowires directly on the Zn substrate and the other is the vapor–solid mechanism that leads to the formation of ZnO powder that is deposited onto the adjacent Si wafer due to evaporation of Zn from the melted Zn.

To further confirm the temperature effect on the ZnO nanosstructure growth described above, detailed transmission electron microscopy (TEM) characterization of the microstructure of the ZnO nanostructures formed at the different temperatures is performed. Fig. 5(a) shows a TEM image of a single ZnO nanowire formed on the Zn foil oxidized at 400 °C. It reveals that the ZnO nanowire contains a bi-crystal boundary at the middle and along the axial direction, as indicated by the white arrows. The high-resolution TEM (HRTEM) image shown in Fig. 5(b) further confirms the bicrystalline structure of the ZnO nanowire. The interplanar spacings of each side of the bicrystalline nanowire as measured from the high-resolution TEM image are both 2.82 Å, corresponding to the calculated lattice spacings of ZnO {10\(\overline{1}0\)}.

A large number of ZnO nanowires were examined using HRTEM, and most nanowires formed from the oxidation at the temperatures below the melting point of Zn exhibit the similar bicrystalline structure. Fig. 5(c) shows an SEM image revealing the growth

![Fig. 5.](image-url)
roots of the nanowires and one can see that the oxidized Zn surface consists of faceted ZnO grains, and ZnO nanowires are grown directly on top of the grains as indicated by the arrow. This growth feature is also confirmed by the cross-sectional TEM image as shown in Fig. 5(d), which demonstrates that the nanowire is formed directly on top of an underlying ZnO grain.

Fig. 6 shows TEM images of a single ZnO nanowire formed on a Zn foil oxidized at 500 °C. Clearly, the nanowire has a needle shape with a diameter of 80 nm at the root and 20 nm at the tip (Fig. 6(a)). Different from the nanowires formed from the oxidation at 400 °C, the TEM image shows that there is no bi-crystal boundary present along the axial direction of the nanowire. This is confirmed by selected area electron diffraction (SAED) pattern as shown in Fig. 6(b), where the zone axis is along ZnO [0001] direction and the pattern can be identified as single-crystal ZnO. Fig. 6(c) displays an HRTEM image, which reveals that the nanowire is single crystalline without the presence of bi-crystal boundaries along the axial axis. TEM examinations of ZnO nanowires formed from the oxidation at 600 °C and 800 °C reveal the similar structure feature, i.e., no bi-crystal boundary present in the nanowires. These TEM observations are also consistent with other published results [27,32].

Fig. 7(a) shows a TEM image of a ZnO nano-tetrapod formed on the silicon substrate from the oxidation at 1000 °C. Fig. 7(b) is a HRTEM image of a single leg of the ZnO nano-tetrapod shown in Fig. 7(a). The crystal lattice fringes indicate the nano-tetrapod leg has a single crystalline structure and grows along the [0001] direction. The SAED pattern obtained from the nano-tetrapod leg further confirms its single crystalline structure. By combining the TEM results as shown in Figs. 5–7, we can conclude that oxidation at the temperatures below the melting point of Zn results in the formation of bicrystalline ZnO nanowires, and the oxidation above the melting point leads to formation of single crystalline ZnO nanowires and ZnO tetrapods with single crystalline legs.

4. Discussion

The experimental results described above reveal clearly that the growth morphologies and microstructures of the ZnO nanosstructures depend on the oxidation temperature. This can be attributed to the temperature-dependent growth mechanisms, as summarized schematically in Fig. 8. We first discuss the formation of ZnO nanowires for oxidation at the temperatures below the melting point of Zn. For the solid–solid transformation induced oxide nanowire formation during the oxidation of metals, it has been shown that the oxide nanowire formation is driven by relaxation of compressive stresses accumulated in the oxide overlayers and oxide nanowires formed by this mechanism typically show the presence of a bi-crystal boundary along the nanowire axial direction [36–41]. In this mechanism, the compressive stress driving the oxide nanowire formation is originated from the metal-oxide interface for single oxide layer growth or the oxide–oxide interface during layered oxide growth (if the metal has multiple oxide phases, e.g., Cu, Fe) due to their volume mismatch associated with the interfacial conversion reaction.
The observed ZnO nanowire formation for the oxidation of Zn at the temperature below its melting point can be understood similarly by the stress-driven mechanism. Owing to the larger molar volume of ZnO than Zn, the transformation of Zn to ZnO generates compressive stress in the ZnO layer adjacent to the ZnO–Zn interface. Since the outer surface of the ZnO layer is stress free, there is a stress gradient across the ZnO layer that drives outward diffusion of Zn ions from the high stress ZnO/Zn interface region to the low stress region of the outer surface for nucleation and growth of ZnO nanowires on exposed ZnO grains. ZnO crystals grown on the adjacent facets of a single ZnO grain are joined to form a bicrystal structure. As described in Fig. 5, the two sides of bicrystalline nanowires have the same type of (10T0) lattice. Since ZnO nanowires grow directly on the exposed surfaces of ZnO grains which serve as the structure template for the nucleation and growth of (10T0) bicrystalline nanowires, the typically observed lattice planes of (10T0) in the nanowires suggest that the exposed surfaces of the ZnO grains are dominated by (10T0). This is very likely because the (10T0) facet has the smallest surface energy among the ZnO surfaces [42]. Further growth of the nanowires occurs via the reaction of Zn ions with oxygen on the nanowire tip, where Zn ions are supplied by surface diffusion along the nanowire wall from the bottom to the tip. Fig. 8 (a) shows schematically the growth process of a bicrystalline ZnO nanowire by this mechanism.

For this mechanism to be operative effectively, the underlying ZnO layer should be sufficiently thin. Our earlier experiments on the oxidation of Cu and Fe showed that the thickness of the top oxide layer (CuO or Fe₂O₃) is less than 1 μm for CuO or Fe₂O₃ nanowire formation [39,41,43]. Otherwise, the stress will be released by other mechanisms such as cracking and delamination of the oxide layer and/or plastic deformation of the oxide and metal substrate if a thick oxide scale develops. This was also confirmed from the oxidation of brass at different temperatures, which showed that the thickening of the underlying ZnO layer suppresses the formation of ZnO nanowires on the outer surface [37]. For oxidation of Zn at the relatively low temperature (400 °C), the thickness of the underlying ZnO layer on which the formation of ZnO nanowires occurs is only about 150 nm (see Fig. 9(a)). This is consistent with the stress-driven mechanism, which requires that the oxide layer be thin enough for effective relaxation of stresses generated at the ZnO/Zn interface. While for Zn oxidation at temperature above the melting temperature (500–800 °C), we also observed ZnO nanowire formation on the thick ZnO layer, where the thickness of the underlying ZnO layer on the Zn substrate varies from 1.2 μm to 1.8 μm (see Fig. 9(b) and (c)). With such a thick ZnO layer, there is still ZnO nanowire formation and the oxide layers also show good adhesion to the Zn substrate without the oxide delamination or crack formation, as seen from the cross-sectional SEM images shown in Fig. 9(b) and (c). This implies that the ZnO nanowire formation at the temperatures above the melting point follows a different mechanism.

For oxidation at temperatures between the melting and boiling points of Zn, the oxide nanowire formation on the Zn substrate can be attributed to a liquid–solid process. At these temperatures, the Zn substrate surface forms a thin layer of liquid Zn. Reaction of the liquid Zn with incoming oxygen forms solid ZnO nuclei on the liquid Zn layer (note that ZnO has a melting point of around 1970 °C and forms as solid precipitates during the oxidation), which serve as seeds for ZnO nanowire formation [27]. The tapered shape of the nanowires (see Fig. 6(a)) suggests that the nanowire growth occurs via surface diffusion of Zn ions along the side wall of the nanowire, which results in simultaneous growth in both the axial and radial directions by reacting with impinging oxygen. The surface diffusion of Zn is driven by the concentration gradients of Zn ions along the nanowire wall from the root region to the tip. This also explains why most nanowires have a coarse root and become thinner at the tip because a significant amount of Zn ions are incorporated into the nanowire near the root region by reacting with impinging oxygen.
At temperature above the boiling temperature of Zn, the formation of ZnO nano-tetrapods is observed as shown in Fig. 7. The growth of ZnO tetrapods have also been observed previously from the oxidation at the similar high temperature [14,44]. The vapor–solid mechanism can be employed to understand the formation of the tetrapod morphology. The Zn substrate rapidly evaporates to form Zn vapor above the boiling temperature. With the inlet flow of oxygen gas, ZnO nuclei start to form by the reaction between Zn vapor and oxygen. It was suggested that ZnO nuclei formed from the vapor reaction adopt an octahedral-twinned shape with exposed (0001) base planes, which minimize the surface energy of the ZnO cluster because of the low surface energy of the basal plane (the surface energy for Zn-terminated base (0001) surface is slightly larger than the (1010) plane) [42,45]. However, after the octahedral multiple twins grow to a larger size, the strain energy due to the misfit angle of the multiple twins leads to the cracking of the twin boundaries and the subsequent growth of the ZnO particle continues preferentially along the [0001] direction due to the larger anisotropy of the growth rate. As a result, a tetrapod ZnO nanostructure is formed by filling up the crack in the octahedral-twinned nucleus, and the variation in the cracking process in octahedral-twinned nucleus may lead to variation in the angles among legs of the ZnO tetrapods. Such a process of tetrapod ZnO formation has been described previously in the literature [44–47]. This mechanism corroborates with our TEM observations of the ZnO tetrapods, which reveal that the axial direction of tetrapod legs is indeed along ZnO [0001] direction, as shown in Fig. 7.

5. Conclusions

The growth morphologies and microstructure of ZnO nanostructures formed from the oxidation of Zn at different temperatures are studied. It is shown that the oxidation below the melting point of Zn results in the growth of bicrystalline ZnO nanowires, single-crystalline ZnO nanowires between the melting and boiling points of Zn, and ZnO tetrapods above the boiling point of Zn. The temperature-dependent growth morphology and microstructure are attributed to the temperature effect on the oxidation mechanism of Zn. For oxidation below the melting point of Zn, the ZnO nanowire formation follows a solid–solid transformation mechanism in which the compressive stress generated from the ZnO/Zn interfacial reaction stimulates ZnO nanowire formation. At temperatures between the melting and boiling temperatures of Zn, the formation of single crystalline nanowire occurs via a liquid–solid mechanism in which liquid Zn reacts with gaseous oxygen to form solid ZnO nuclei that grow anisotropically via surface diffusion of Zn. The formation of ZnO nano-tetrapods at the temperature above the boiling temperature of Zn follow a vapor–solid mechanism in which the tetrapod ZnO growth occurs by filling up cracks in octahedral-twinned nuclei.

Acknowledgments

This work was supported by the National Science Foundation under Grant no. CMMI-0825737. Y.Q. Wang would like to thank the financial support from the National Natural Science Foundation for Outstanding Young Scientists in Shandong Province, China (Grant no JQ2010002). We thank Mr. Shawn Wagoner for the help with gold deposition on Si.

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