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

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ABSTRACT

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

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

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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 with pure oxygen (99.999%) as the reaction gas. Zn samples are first thoroughly rinsed with deionized water followed by ultrasonication in acetone for 5 min. The cleaned Zn substrate is dried in N_2 and then placed in a ceramic boat. The silicon substrate is placed in another ceramic boat. Those two ceramic boats are then put into the horizontal tube furnace with the silicon substrate upstream along the gas flow direction. Fig. 1 is a schematic diagram of the experimental setup. The purpose of placing a Si substrate next to the Zn foil is to examine if there is any ZnO nanostructure deposition onto the surrounding area, particularly upstream along the oxygen gas flow direction, which would provide significant insight regarding the vapor–solid mechanism for ZnO nanostructure formation during the oxidation of Zn. Before the oxidation experiment, the furnace is flowed with 100 sccm (standard cubic centimeter per minute) argon (Ar) gas for 5 min and then rapidly heated from room temperature to the desired temperature ranging from 200 °C to 1000 °C in 10 min with Ar gas flow. The oxidation of Zn is performed by switching quickly from the Ar gas flow to pure oxygen gas flow with a 100 sccm flow rate and the oxidation duration is 30 min. After oxidation, the furnace is then naturally cooled down to room temperature in the oxygen atmosphere. The as-synthesized products are characterized by field emission scanning electron microscopy (FEG-SEM, FEI Supra 55VP) and transmission electron microscopy (JEOL JEM 2100 F) operated at 200 kV.

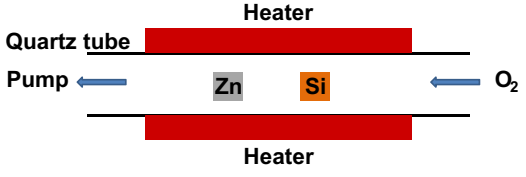

Fig. 1. Schematic illustration of the experimental setup for the oxidation of Zn.

3. Results

Fig. 2 shows representative SEM images of the surfaces of the Zn foils oxidized at the different temperatures. The SEM observations show that no ZnO nanostructures are formed on the Zn substrate at relatively low oxidation temperatures (200 °C and 300 °C) (see Fig. 2(a) and (b)). The oxidation at 400 °C results in the formation of ZnO nanowires on the Zn surface, where the diameter of the nanowires is ~20 nm and the length is up to 500 nm (see Fig. 2(c)). As seen in Fig. 2(d), the oxidation at 500 °C results in the formation of ZnO nanowires with a much higher surface density, larger diameter (~50 nm) and longer length (~1.5 μm) compared to the lower oxidation temperature. Fig. 2(d) also shows that the oxidized Zn substrate becomes slightly roughened compared to the oxidation at the lower temperatures, which may be caused by surface melting of the Zn substrate at the oxidation temperature (the melting temperature of Zn is ~420 °C). For oxidation at 600 °C, the Zn surface becomes highly roughened with formation of taper-shaped ZnO nanowires having a diameter of 500 nm at the root and a length up to 2 μm (Fig. 2(e)). For oxidation at 800 °C, micro-sized ZnO rods are formed on the significantly roughened Zn surface. Those rods are tapered with a diameter up to 1.8 μm at the root region and a length up to several μm, indicating the significant radial growth in addition to the axial growth. For oxidation at 1000 °C, the Zn foil has totally disappeared from the ceramic boat where the Zn foil was originally placed, this is due to the fast evaporation of Zn at the high temperature above its boiling point (907 °C).

As described in the experimental section, another ceramic boat with a Si wafer inside was also placed next to the ceramic boat with the Zn foil inside. Examining the reaction product on the Si wafer would allow for elucidating if the vapor–solid process is involved in ZnO nanostructure formation, for which Zn is expected to evaporate from the Zn foil and reacts with oxygen gas to form ZnO nanostructures which are then deposited onto the Si wafer. Fig. 3 shows representative SEM images of the surface morphology of the Si substrates. For oxidation at the relatively low temperatures of 300 °C and 400 °C (i.e., below the melting temperature of Zn, 420 °C), the silicon surfaces are clean without any ZnO nanostructure formation. For oxidation at the temperatures of 500 °C and 800 °C, which are between the melting and boiling points of Zn, discontinuous ZnO thin films are formed on the Si surface and the oxide films become more continuous at the higher temperature (note that the Si surfaces do not show any ZnO nanowire structures except for the observed ZnO thin films). For the oxidation at 1000 °C, there is a high density of ZnO nano-tetrapods formed on the Si surface. As seen in Fig. 3(f), each ZnO nano-tetrapod contains four legs with a diameter of ~500 nm and the length of ~2 μm. The legs have smooth surface and a sharp tip at the end.

It is reasonable to assume that the formation of ZnO thin films on the silicon substrates is due to deposition of ZnO formed from oxidation of Zn vaporized from the Zn foil. The barely visible ZnO formation on the Si substrate for oxidation at 300 °C and 400 °C suggests that very few Zn is vaporized and ZnO forms directly on the Zn foil via the solid–solid transformation (i.e., solid Zn is oxidized to from a solid ZnO coating on the Zn substrate). For oxidation at the temperatures (i.e., 500 °C, 600 °C, and 800 °C examined in our experiments) above the melting point of Zn, a liquid Zn layer should form on the surface of the Zn foil, which promotes the evaporation of Zn. The reaction of Zn vapor and oxygen results in the formation of solid ZnO powders which are