Electron Beam Induced Growth of TiO$_2$ Nanostructures

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We report the evolution of titanium dioxide nanostructures when Au nanoparticles, supported on single crystal TiO$_2$ substrates, were heated under ~260 Pa of flowing O$_2$ in an environmental transmission electron microscope. Nanostructures with different morphologies were first observed around 500°C. Our measurements show that temperature, oxygen pressure and the electron beam control the nanostructure growth. We propose a reaction-controlled growth mechanism where mobile Ti atoms generated

by the electron beam induced reduction of TiO$_2$, are preferentially re-oxidized at the Au-TiO$_2$ interface.

INTRODUCTION

Titanium dioxide (TiO_2) is a versatile material and has been extensively investigated due to its current and potential applications in several industrially relevant processes such as photocatalysis, photovoltaics, gas sensors and metal catalyst supports (Diebold, 2003). It is generally accepted that the performance of TiO_2 can be improved in nanostructures due to the increase in surface area (Chen & Mao, 2007). For example, Khan & Sultana (2003) showed that the photo-conversion efficiency for hydrogen production improved by more than 2-fold from water and 4-fold from methanol, respectively by replacing TiO_2 films with nanowires. Currently, one dimensional (1-D) TiO_2 nanostructures are primarily synthesized via chemical methods such as sol-gel and anodic oxidation, but the crystallinity of as-synthesized nanostructures produced by these techniques is poor and undesirable contamination is often present. Therefore, the direct vapor-based synthesis of 1-D nanostructures on compatible substrates is preferred for them to be integrated into device fabrication. To date, TiO_2 nanowires have been successfully synthesized on sapphire (Wu et al., 2006), alumina (Wu et al., 2005a) and silicon (Wu et al., 2005b, Xiang et al., 2006, Lee et al. , 2006, Baik et. al, 2008) using physical vapor deposition; both with and without a metal catalyst. A pre-deposited Ti layer (that was oxidized to TiO_2) and a secondary Ti source were required for synthesis in the reported results. Nonetheless, research in this area is still in its early stages and the growth mechanism of these nanostructures is still not well understood.

In this paper, we report the growth of one-dimensional TiO_2 nanostructures when Au nanoparticles supported on single crystal TiO_2 substrates were heated under flowing

oxygen in an environmental transmission electron microscope (E-TEM). Recent experimental studies using similar *in situ* setups had been successfully employed to elucidate the growth dynamics of a number of nanostructures such as carbon nanotubes (Sharma et. al, 2007), silicon (Kodambaka et al., 2006) and germanium (Kodambaka et al., 2007) nanowires. Using *in situ* experiments, we found that our nanostructures do not grow by a vapor-liquid-solid (VLS) mechanism (Wagner & Ellis, 1964) and instead propose a solid-state mechanism to account for their formation. Furthermore, our results show that the formation of nanostructures is driven by the surface diffusion of excess Ti atoms or TiO_x molecules. This process can be a possible mechanism for physical vapor synthesis.

MATERIALS AND METHODS

The experiments were carried in a modified FEI Tecnai F20[*] operated at 200 KV and equipped with a differentially pumped environmental cell (Sharma, 2005). The substrates were rutile TiO_2 (110) single crystal wafers purchased from MTI Crystal Corporation[*]. The wafers were first cut to 3mm discs and ground to ≈ 20µm thickness by dimpling. Electron transparent regions were produced by ion-milling. The discs were heated to $1000^{\circ}C$ for 30 min in an air furnace to remove the specimen damage introduced by ion-milling. This led to the crystallization of TiO_2 with well defined terraces and steps edges parallel to the electron probe direction. Gold was deposited on the discs by sputtering and subsequently heated to $500^{\circ}C$ in air to promote coarsening and epitaxy between Au and

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[*] *Disclaimer: The full description of the procedures used in this paper requires the identification of certain commercial products and their suppliers. The inclusion of such information should in no way be construed as indicating that such products or suppliers are endorsed by NIST or are recommended by NIST or that they are necessarily the best materials, instruments, software or suppliers for the purposes described.*

TiO$_2$. The resultant Au nanoparticles were about 4 nm in size. During the experiment, the discs were heated in ≈ 260 Pa (2 Torr) to 670 Pa (5 Torr) flowing O$_2$ up to 710 $^{\circ}$C in the E-TEM. Digital videos were recorded to observe the growth process of the nanostructures using a Gatan Orius 600SC[*] camera with a time resolution of 15 frames s^{-1}[*]. The imaging was done along the <110> zone axis of the TiO$_2$ and an estimated dose rate of ≈ 8 x 10^4 electrons per nm^2 per s at x195k (Figure 1 and 2), ≈ 1.2 x 10^5 electrons per nm^2 per s at x285k (Figure 3) and ≈ 3.7 x10^5 electrons per nm^2 per s at x400k (Figure 4) was maintained during observations.

RESULTS AND DISCUSSION

Figure 1 shows a series of images extracted from the video (provided as supplementary material 1) recorded at 532 $^{\circ}$C and in 283 Pa of O$_2$. Initially, only Au nanoparticles were present; however, TiO$_2$ nanostructures begun forming around the nanoparticles after ≈ 7 s. Pronounced nanostructures could be observed after 21 s (Figure 1b) and after 55 s, three different morphologies were found coexisting in this area (Figure 1c). The nanostructures are defined as (1) an island when it grows laterally along the edge of the substrate, (2) a wire when it grows extensively along a direction away from the substrate and (3) a plate when there is both lateral and vertical growth. We emphasize here that in all instances, the growth of nanostructures was observed to begin at temperatures above 520°C in 285 Pa O$_2$ only when a particular area of the sample is moved into the electron beam.

In Figure 2, the image series show the nanostructure growth at 656 $^\circ$C in 297 Pa of O_2 from two separate areas of the sample (digital videos provided as supplementary material 2 and 3). In area 1, two structures can be seen; marked as plate and wire growth (4 and 5 in Figure 2a) respectively. Initially, the Au nanoparticle was observed to be mobile on the surface of the TiO_2 plate-shaped nanostructure, but it became immobilized after it reached the position shown in 2(c). Area 2 shows a growing wire and in this sequence, lateral growth of the wire via step flow (as highlighted in 2(e)-(f)) was observed. The measured increase in the projected areas of the nanostructures labeled 2 to 6 in Figures 1 and 2 is plotted versus time in Figure 5. The projected area was used to compare the growth rates between the two morphologies and the increase was measured with reference to Figures 1(b), 2(a) and 2(d). The growth rate is higher for the structures formed at 656 $^\circ$C compared to those at 532 $^\circ$C. The linear growth rates of the wires 2, 5 and 6 were calculated to be 0.19 ± 0.01 nms^{-1}, 0.78 ± 0.06 nms^{-1} and 1.10 ± 0.05 nms^{-1} respectively. In general, our measurements show that the growth rates increased with temperature.

Figure 3 is extracted from a video recorded at 712 $^\circ$C, in 335 Pa O_2 which shows the TiO_2 support disintegrating after about 1 min of exposure to the electron beam. This indicates that electron beam damage plays a significant role in removing material during our experiments. Previously, the electron beam induced damage to TiO_2 surfaces was investigated using an ultrahigh vacuum TEM (McCartney and Smith, 1991). The authors reported that the damage increased with temperature and well-facetted holes were observed above 500°C. This void formation is similar to what we observed above 710 $^\circ$C.

On the other hand, no nanostructure growth was observed when the O_2 pressure was raised to 670 Pa with the temperature kept at $\approx$ 600 $^\circ$C. Lastly, inspection of the sample after the experiment showed that no nanostructures were formed outside the areas that had not been irradiated by the electron beam. It is safe to conclude that the nanostructures form when the following three conditions are satisfied: (a) The temperature is between 500 $^\circ$C to 700 $^\circ$C; (b) O_2 partial pressure between 260 Pa to 670 Pa and (c) the sample is irradiated by the electron beam. To explain our observations, we present the following solid state mechanism (depicted in Figure 6) rather than VLS to explain the observed TiO_2 nanostructure formation.

First of all, to account for TiO_2 formation in the absence of an external Ti source, we propose that the observed growth is due to a dynamic equilibrium between TiO_2 reduction induced by electron beam and preferred re-oxidation of Ti atoms at the Au-TiO_2 interface. The model is based on the following propositions

a) An excess of Ti atoms or TiO_x molecules is generated by an electron beam induced reduction of the TiO_2 surface.

b) The temperature is high enough for the reduced Ti species to be mobile on the crystal surface.

c) The oxygen pressure is such that a dynamic equilibrium is established between the surface reduction and re-oxidation of the TiO_2.

d) There is preferential re-oxidation taking place in the vicinity of the Au nanoparticle.

It is well-known that the surface of TiO_2 crystals reduces during annealing at high temperature in vacuum (Diebold, 2003). Previous studies using transmission electron microscopy also found that electron radiation damage can also reduce TiO_2 to TiO or even metallic Ti (Smith et. al, 1987, McCartney et. al, 1991). On one hand, existing literature about the re-oxidation of reduced single crystal TiO_2 surface (Li et. al, 1999, Smith et.al, 2002) has shown that the diffusion of interstitials from the bulk can also lead to changes in the surface morphology. While this may be a possible source of the Ti atoms, we do not believe it to be the primary source for the following reasons. The sample has been annealed in air prior to Au deposition at 1000°C and does not exhibit the characteristic purple color of partially reduced TiO_2. Nanostructures were not observed in samples after the second anneal at 500°C in air after Au deposition and were also not observed in areas not illuminated by the electron beam. Therefore, we assume that the Ti source for nanowire growth is primarily the electron beam induced reduction of the substrate crystal itself. Although the *ex situ* studies on the surfaces of reduced TiO_2 crystals annealed in vacuum (Henderson, 1999) and in oxygen (Li et. al, 1999) from 200 °C to 560 °C support both the mobility and re-oxidation of Ti atoms at our experimental temperatures, we expect that the surface migration of the Ti species, generated by electron beam induced reduction; at elevated temperatures to dominate over bulk diffusion of Ti interstitials. The nucleation of TiO_2 on the clean surfaces of the nanostructures; such as the step flow observed in Figure 2, provides further evidence of the surface diffusion of Ti atoms. While we believe that surface diffusion is the dominant transport mechanism, we also do not rule out the vapor transport of Ti atoms created by electron beam sputtering (Egerton et. al, 2006).

While it is clear that the Au nanoparticles direct the growth of these nanostructures, the exact role of the nanoparticles remains unclear. One possibility is the metal-support interactions that are commonly observed for metal nanoparticles on titanium dioxide; for example, the dissociation of oxygen on Pd surface is known to cause a "spillover" effect where TiO_2 re-grows around the Pd nanoparticle (Bennett et. al, 1999). It is more likely that the Au plays role of a traditional catalyst by providing a kinetically favorable pathway for re-oxidation. While experimental studies had shown that molecular oxygen does not readily adsorb on the Au surface (Cosandey and Madey, 2001), density functional theory calculations by Liu et. al (2003) had indicated that the Au-TiO_2 interface may be a favorable site for the adsorption and dissociation of O_2. In current models for the growth of nanowires, it is also generally accepted that there has to be preferential nucleation of the growth species at the catalyst-substrate interface (Wacaser et. al, 2009). In the case of our experiments, this preferential nucleation may be in the form of enhanced adsorption of oxygen at the Au-TiO_2 interface.

In the growth stage of the model (Figure 6), we propose that the nanostructure formation takes place in the following steps. Initially, an epitaxial base forms as new material nucleates at the Au-TiO_2 interface. This can be clearly seen from high resolution images in Figure 4. Lattice spacings obtained from fast Fourier transform (FFT) of the images confirm the structures to be rutile (Joint Committee on Powder Diffraction Standards (JCPDS): 00-021-1276, TiO_2, rutile). As observed from the videos, the Au nanoparticle is mobile on the TiO_2 surface and is able to move along the different surface facets as the

nanostructure grows. While the TiO_2 growth only took place in the vicinity of a nanoparticle, it was not limited to a certain crystal facet (i.e. plate morphology in Figures 1 and 2). Some facets; such as (110) for rutile TiO_2, are known to be more favorable for growth than others. We expect that when the nanoparticle moves onto these facets, there will be uni-directional growth that leads the formation of the nanowire morphology.

In order for nanostructure growth to take place at the interface, the re-oxidation reaction has to be kinetically limited by the pressure of oxygen; i.e. the Ti atoms must not be re-oxidized before they diffuse to the Au-TiO_2 interface. Higher temperatures and oxygen pressures within a narrow window present the ideal conditions required for establishing the dynamical equilibrium required for growth. At lower temperatures, the lack of nanostructure growth can be attributed to a lower surface diffusion rate of Ti atoms to the Au-TiO_2 interface. At higher O_2 pressures, the electron beam-reduced Ti atoms will become immobile due to instantaneous re-oxidization. This explains why nanostructure formation was suppressed at higher O_2 pressures and is consistent with previous work by Amin et. al (2007) on the synthesis of TiO_2 nanostructures from nickel-coated TiO powders. Interestingly, they found that when rutile and anatase TiO_2 powders are used, there was no nanostructure growth and agree with our assertion that TiO_2 needs to be in the reduced state. Lastly, since re-oxidation cannot take place in the absence of O_2; TiO_2 nanostructures were not observed to form during imaging in vacuum even at elevated temperatures.

To summarize, the formation of the nanostructures is initiated by the electron beam and hence, provides us with the ability to monitor the entire growth process. Furthermore, the growth conditions that were identified from the *in situ* experiments may be extended to the *ex situ* synthesis of TiO_2 nanostructures on single crystal TiO_2. The technique outlined here can be applied to the study of other metal oxides. The fabrication of 1-D metal oxide nanostructures is an area of intensive research due to their tunable physical properties and potential applications in nanoscale devices (Xia et. al, 2003, Dai et. al, 2003). While a wide variety of nanostructures such as nanowires, nanoribbons, nanodisks had been synthesized, there is still much to learn about how these different morphologies evolve.

CONCLUSIONS

In conclusion, we were able to grow 1-D TiO_2 nanostructures on TiO_2 single crystal substrates without an external Ti source in an E-TEM and observe the entire growth process *in situ*. The growth was observed between $500^{\circ}C$ and $700^{\circ}C$, under ~2 Torr flowing O_2 and only under the electron beam. We propose that the growth mechanism is a reaction-controlled process where Ti atoms generated by the electron beam damage of the TiO_2 surface are preferentially re-oxidized at the Au-TiO_2 interface. The observations are consistent with *ex situ* results. The synthesis parameters that we identified can possibly lead to alternate methods for fabricating TiO_2 nanostructures.

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Figures and Captions

Figure 1 Time series images extracted from digital videos recorded at 532°C, 283 Pa (2.12 Torr). The three morphologies labeled in 2(c) are; (1) Island, (2) Wire and (3) Plate.

Figure 2 Time series images extracted from digital videos recorded at 656°C, 297 Pa (2.23 Torr). 2(a)-(c) and 2(d)-(f) are from 2 different areas of the sample. Arrows in 3(e) highlight two steps which propagated towards each other and merged by 3(f).

Figure 3 Single image extracted from a digital video recorded at 712°C, 335 Pa (2.51 Torr) showing the disintegration of the TiO_2 after about 1 min exposure to the electron beam.

Figure 4. High resolution images extracted from videos recorded at 600°C, 260 (2 Torr) O_2 and the FFT from the respective highlighted areas. The measured lattice spacing agree well with that of the (001) and (110) planes of rutile TiO_2.

Figure 5 Plot of the increase in projected area versus time for the nanostructures labeled 2-6 in Figures 1 and 2.

Figure 6 Schematic depicting the three-part process of nanowire growth; (1) reduction of TiO_2 surface generating mobile Ti atoms, (2) collection of Ti atoms at the Au/TiO_2 interface followed by re-oxidation forming the epitaxial base and (3) nucleation of new material at the interface leading to nanostructure growth.