Enhanced CuO Nanowire Formation by Thermal Oxidation of Roughened Copper

Lu Yuan and Guangwen Zhou

Email alerting service	Receive free email alerts when new articles cite this article - sign up in the box at the top right corner of the article or click here

Enhanced CuO Nanowire Formation by Thermal Oxidation of Roughened Copper

Lu Yuan and Guangwen Zhou[z]

*Department of Mechanical Engineering & Multidisciplinary Program in Materials Science and Engineering,
State University of New York, Binghamton, New York 13902, USA*

By exerting sandblasting onto copper surfaces, we show that increasing the surface roughness can effectively promote CuO nanowire formation by significantly enhancing the nanowire growth density and length during the oxidation of copper. It is found that the enhanced nanowire nucleation and growth is associated with the increased thickness of the underlying CuO and Cu_2O layers and decreased grain sizes of the two oxide layers. These results demonstrate that the increased surface roughness of the metal substrate results in finer grain structures in the layered oxide growth, thereby facilitating outward diffusional transport of Cu atoms along grain boundaries for enhanced CuO nanowire formation.
© 2012 The Electrochemical Society. [DOI: 10.1149/2.102204jes] All rights reserved.

One-dimensional (1D) metal-oxide nanostructures such as nanowires, nanobelts, nanotubes, and nanorods, have attracted much attention due to their unique properties and potential technical applications. Understanding the mechanisms controlling the nanowire growth is a critical topic of fundamental study that allows for precise control of the growth processes for achieving desired properties and applications. Various approaches have been employed to generate 1D oxide nanosturctures including physical and chemical routes, such as vapor-liquid-solid growth, epitaxial growth, vapor-solid growth, wet chemical methods, and electrospining.[1] Compared to these methods involving relatively complex and multi-step synthesis procedures, oxide nanowire formation by direct thermal oxidation of metals is a simple approach with large-scale growth capabilities. Particularly, the formation of CuO nanowires by oxidation of copper represents the most representative examples due to the potential broad applications of nanostructured CuO. CuO (cupric oxide) is a p-type semiconductor with narrow bandgap of 1.4 eV.[2] A number of interesting properties have been found in this p-type semiconductor material that have led to its myriad technological applications in important fields including solar energy conversion,[3] photocatalysts,[4] fuel cells,[5] emission control,[6] cathode materials in lithium ion batteries,[7] gas sensing,[2] and heterogeneous catalysis for hydrocarbons conversion reactions.[8]

Oxide whisker formation from the oxidation of metals is a long-established phenomenon dating back to the 1950s,[9] but only recently has received significant attention in the field of nanotechnology.[10–12] The oxidation of metals to form oxide nanowires typically requires the sequent growth of multiple and parallel oxide layers followed by the subsequent growth of oxide nanowires on the top oxide layer. For instance, the oxidation of copper results in multiphase scales of Cu_2O and CuO on Cu. It has been shown that the oxide scale growth obeys the parabolic rate law controlled by the outward of Cu ions via Cu vacancies.[13–15] While oxide layering can be understood from thermodynamic equilibrium analysis, the understanding of the mechanism governing the oxide whisker formation accompanying the layered oxide growth is still far from complete. Several mechanisms have been proposed based on different observations, such as vapor-solid (VS) model,[16] short-circuit diffusion up the center of the nanowires,[17] or surface diffusion along the sides of nanowire.[18,19] Since the formation of highly volatile oxide species actually does not occur for the intermediate oxidation temperatures at which CuO nanowires grow, the VS model seems not to apply to the oxide whisker. Recent electron microscopy observations reveal that CuO nanowires have a bicrystal or single crystal structure (i.e., no hollow pipe present along the axial core of nanowires), the fast internal diffusion mechanism is also debated.[19] Alternatively, the stress-driven oxide whisker growth mechanism has been invoked to understand oxide whisker growing

during the oxidation of metals.[19–21] Due to their different molar volumes between the various oxide phases, the ensuring difficulties in local volume accommodation give way to the generation of stresses at the interface region between the different oxide phases, which stimulates oxide nanowire growth to accompany the interface reaction via promoting grain boundary diffusion for initiating the nucleation and uniaxial growth of oxide nanowires on the outmost surface.[19–21]

The stress gradient due to the volume changes accompanying the interfacial reaction results in a flow of material to the low stress surface for nanowire growth. The magnitude of the stress gradient is dependent on the rate of the interfacial reaction between the different oxide phases, which is controlled by the outward diffusion of metal atoms through grain boundaris. Therefore, the growth of oxide nanowires is closely related to the grain boundary diffusion in the oxide layers. To date, however, there has been no straightforward experimental verification of the hypothesis that the nanowire formation is a grain-diffusion controlled phenomenon. In this work we provide such a verification experiment in which sandblasting is applied to Cu surfaces to modify the surface roughness, thereby modifying the oxide nanowire formation from the subsequent Cu oxidation. Our results here demonstrate that the increased Cu surface roughness by sandblasting results in a fine grain structure in the oxide layers, which correspondingly facilitates the outward diffusion of Cu atoms and hence enhances Cu_2O/CuO interfacial reaction, thereby promoting the CuO nanowire formation. This work also provides a simple approach for efficiently promoting oxide nanowire formation by thermal oxidation of metals.

Experimental

High-purity copper substrates (99.99%) with a thickness of 0.25 mm are used in the oxidation experiments. In order to study the influence of the surface roughness on the oxide nanowire formation from the oxidation, the copper foils are first sandblasted with different durations to generate different surface roughness. The surface roughness of the sandblasted Cu is measured using an optical profiler (WYKO NT1100). The sandblasted samples are then cleaned with 0.1 M HCl to remove the native oxide layer and then thoroughly rinsed with deionized water followed by ultrasonication in acetone for 5 min. The cleaned Cu substrates are dried in N_2 and then placed on a substrate heater in a vacuum chamber and the sample temperature is monitored using a K-type thermocouple in contact with the substrate heater. The oxidation loading apparatus is large enough so that Cu specimens with different surface roughness can be loaded simultaneously and then oxidized under the same oxidation conditions. The oxidation chamber is first pumped to vacuum ($\sim 2\times10^{-6}$ Torr), and then filled with 200 Torr oxygen pressure (the purity of oxygen is 99.999%). The chamber is then sealed and the Cu sample is heated to 450°C at the rate of $\sim$ 20°C/min and oxidized at the temperature

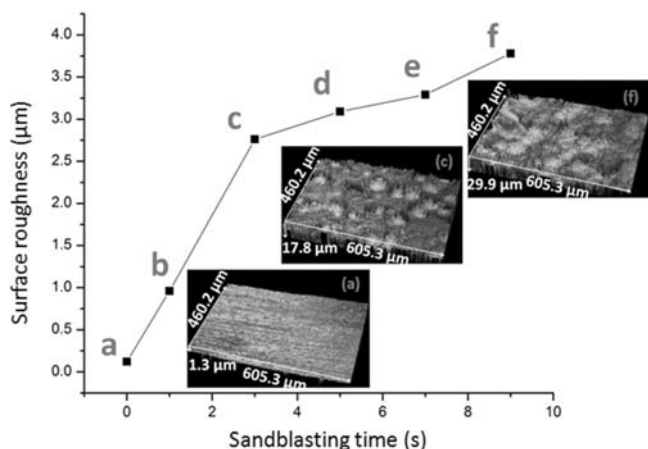[z] E-mail: gzhou@binghamton.edu

Figure 1. Surface roughness Ra vs. sandblasting time. (a), (c), and (f) are 3D surface images taken by profilometer showing the surface morphology of the samples sandblasted for 0 s, 3 s, and 9 s, respectively.

Figure 3. Dependence of the nanowire density and growth length on the surface roughness of the Cu substrates.

for 1 h. It is then cooled down in the same oxygen atmosphere to room temperature at the rate of $\sim 10°C/min$. Growth morphology of the oxidized samples is examined using a field emission gun scanning electron microscope (FEG-SEM) FEI Supra 55VP. Density of CuO nanowires is measured from top-view SEM images; length of CuO nanowires and thickness of the oxide layers are measured from cross-sectional SEM images.

Experimental Results

The surface roughness of the sandblasted Cu substrates is measured by the optical profiler. Fig. 1 shows the surface roughness of the copper substrates after being sandblasted with the different durations. It can be seen that surface roughness increases with increasing the sandblasting time. Image (a) in Fig. 1 shows the optical profiler 3D surface morphology of the copper without sandblasting (i.e., 0 s, corresponding to point a in the plot), where the surface roughness is $\sim 0.12~\mu m$. Image (c) and (f) are 3D surface morphologies of the samples sandblasted for 3 s and 9 s, corresponding to points c and f in the plot, where the roughness is increased to 2.76 μm and 3.78 μm, respectively.

The sandblasted samples are then oxidized simultaneously under the same conditions. The surfaces of all the Cu substrates turn black
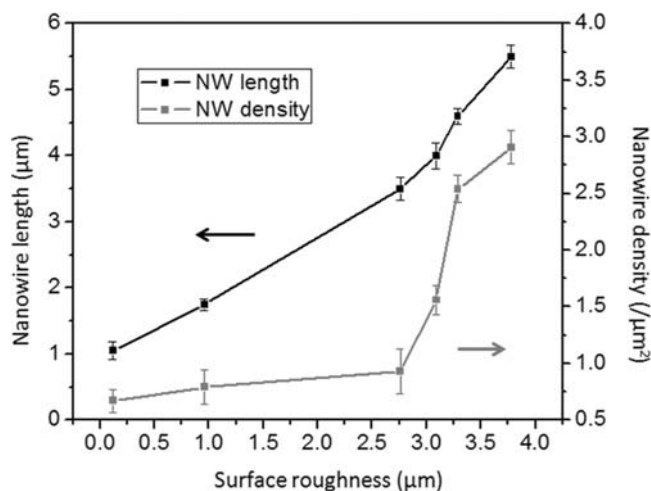
after the oxidation, suggesting that the surface oxide is CuO, which is black in color. Fig. 2 shows representative SEM images of the growth morphology of CuO nanowires on the different Cu substrates oxidized at 450°C, 200 torr for 1 h. Figs. 2A–2C are top-view and Figs. 2D–2F are side-view SEM images of the Cu substrates with the surface roughness of 0.12 μm, 2.76 μm and 3.78 μm. It can be seen from the top-view images that CuO nanowires are formed on the surface. The side-view images show that CuO nanowires are relatively perpendicular to the substrates at their roots.

The diameters of CuO nanowires grown on these surfaces show no noticeable difference and are all in the range of 20 nm$\sim$150 nm. However, the surface density and length of CuO nanowires show obvious dependence on the surface roughness, i.e., they both increase with the surface roughness. To obtain quantitative trend, more copper samples with different surface roughness are oxidized and the results are plotted in Fig. 3. As can be seen, both the density and length of CuO increase with increasing the surface roughness of Cu substrates. The observations reveal evidently that the increased Cu surface roughness promotes the oxide nanowire formation by significantly increasing the nanowire nucleation density and growth length.

In line with previous studies,[22–24] the formation of CuO nanowires on all these Cu surfaces involves Cu_2O/CuO double layer growth with Cu_2O being the bottom layer and CuO being the top layer. However,
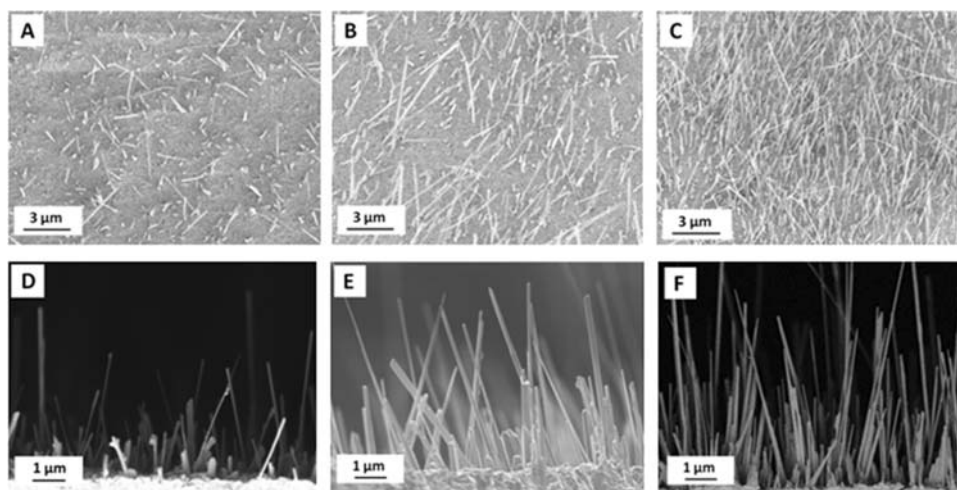

Figure 2. Top view (A, B, C) and side view (D, E, F) SEM images of Cu substrates. A, D: the surface without being sandblasted; B, E: the surface sandblasted for 3 s; C, F: the surface sandblasted for 9 s.
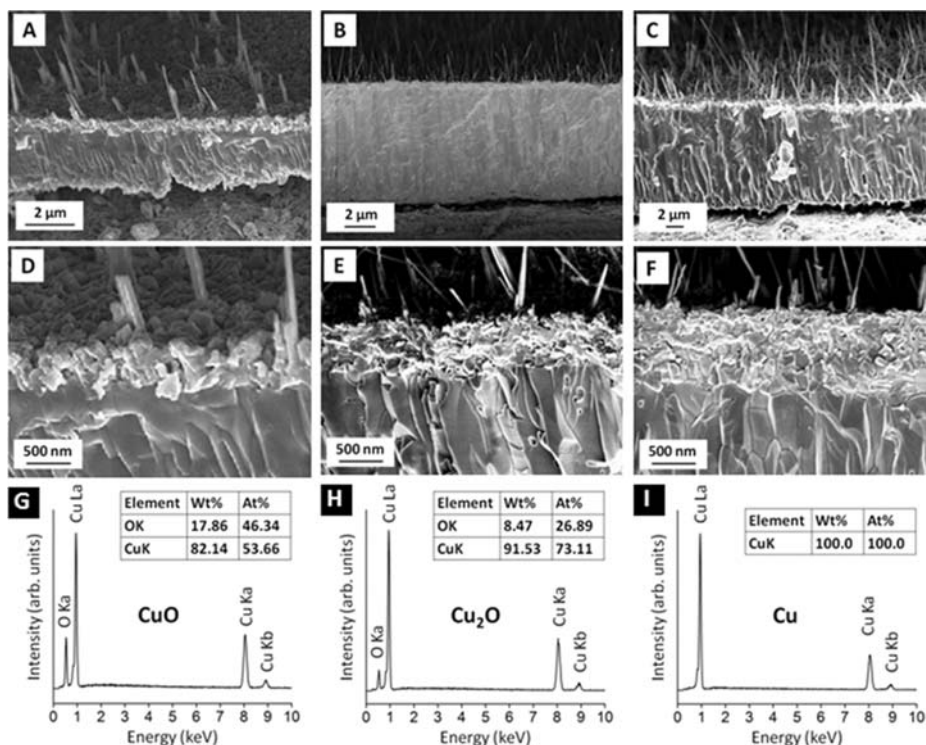
Figure 4. Interface SEM images showing the thickness of Cu_2O and CuO layers formed on the Cu substrates, (A, D): without sandblasting; (B, E): sandblasted for 3 s; (C, F): sandblasted for 9 s. A, B, C are low-magnification SEM images showing the overall morphology of the interfaces of Cu_2O/Cu and CuO/Cu_2O; and D, E, F are high-magnification SEM images from the CuO/Cu_2O interface of the three samples; G, H, I are the EDS spectra and the obtained compositions from the different layers of CuO, Cu_2O and Cu.

the microstructure and thickness of the underlying oxide layers is observed to show dependence on the surface roughness of the Cu substrates. Fig. 4 shows representative cross-sectional SEM images of the oxidized copper substrates. Figs. 4A–4C are low-magnification SEM images revealing the growth of the two oxide layers with the inner Cu_2O layer in contact with the Cu substrate and the outer CuO layer in contact with the oxide nanowires. Figs. 4D–4F show higher magnification SEM images from the Cu_2O/CuO interface areas. The compositions of these oxide layers are determined by X-ray energy dispersive spectroscopy (EDS) analysis as shown in Figs. 4G–4I, which confirms the formation of the inner Cu_2O layer and outer CuO layer. According to the copper-oxygen phase diagram,[25] CuO becomes thermodynamically more favorable than Cu_2O under the large oxygen pressure (>10 Torr) at the intermediate oxidation temperature, which may result in the growth of the CuO oxide layer directly on the Cu substrate. For instance, it was observed that the oxidation of Cu at 400°C under the oxygen gas pressure of 760 torr results in the initial formation of a thin layer of CuO on a Cu surface followed by the nucleation and growth of Cu_2O beneath the CuO layer due to the significantly reduced oxygen pressure at the Cu/CuO interface.[26, 27] However, it should be noted that in our experiments the Cu samples are heated from room temperature to 450°C in a chamber which is prefilled with 200 Torr of oxygen gas. Therefore, oxidation of the Cu surfaces starts actually at a much lower temperature that favors Cu_2O formation directly on the Cu surface, as shown by the copper-oxygen phase diagram.[25]

The growth morphology and grain size of the oxide layers can be also compared from the cross-sectional SEM observations of the roughened Cu samples. For all the cases, the Cu_2O bottom layers contain columnar larger grains while the CuO layer consists of finer grains. Several trends can be noted from their comparisons. The average sizes of grains in both the Cu_2O and CuO layers decrease with increasing the Cu surface roughness. Fig. 5A shows the measured dependence of the grain sizes on the Cu surface roughness, where the oxide grain sizes are estimated from cross-sectional SEM images by measuring the lateral sizes of individual grains. The thickness of the CuO and Cu_2O layers measured from the cross-sectional SEM images is found to increase with increasing the surface roughness of the Cu substrates, as shown in Fig. 5B. The uncertainty ranges given in

Fig. 5 correspond to the range of variation of the quantities measured from different sample areas.

Discussion

An apparent trend revealed from our experiments is that increasing the surface roughness of the Cu substrates effectively promotes the oxide nanowire formation during the oxidation of Cu by enhancing the surface density and growth length of CuO nanowires. It is also found that the thickness of the underlying CuO and Cu_2O layers increases while the average grain sizes of the two oxide layers decreases with increasing the surface roughness of Cu. Such trends demonstrate clearly that the formation of CuO nanowires is intimately related to the microstructure and growth behavior of the underlying Cu_2O and CuO layers, which are strongly influenced by the surface roughness of the Cu substrates, as revealed in Figs. 4 and 5.

We have shown previously that the formation of CuO nanowire is associated with individual CuO grains in the CuO layer, i.e., CuO nanowires nucleate and grow directly on the top of CuO grains, CuO grains serve as the structure template for the nanowire formation.[19] It should be noted that both the Cu_2O and CuO layers grow simultaneously during the oxidation and growth of the Cu_2O layer requires decomposition of the oxygen-richer CuO layer at the Cu_2O/CuO interface. Therefore, for prolonged oxidation, continued growth of the outer CuO layer gradually buries CuO nanowires while growth of the inner Cu_2O layer consume the CuO phase underneath the CuO nanowires, which eventually results in direct contact of the roots of CuO nanowires with the inner Cu_2O layer. Such a growth process of the oxide nanowires can explain well why CuO whiskers are buried by the CuO layer and their roots stem from the Cu_2O/CuO interface area for the prolonged oxidation.[28] The formation of CuO nanowires directly on top of CuO grains thus imposes a correlation between the surface density of CuO nanowires and the density of underlying CuO grains. For a surface with increased nanowire density, an enhanced density of CuO grains is expected, which implies expectations of CuO grains with reduced grain size. These expected correlations are consistent with our observations as shown in Figs. 4 and 5.

Since CuO nanowires are formed directly on the top of CuO grains that grow on the inner Cu_2O layer, the growth behaviors of
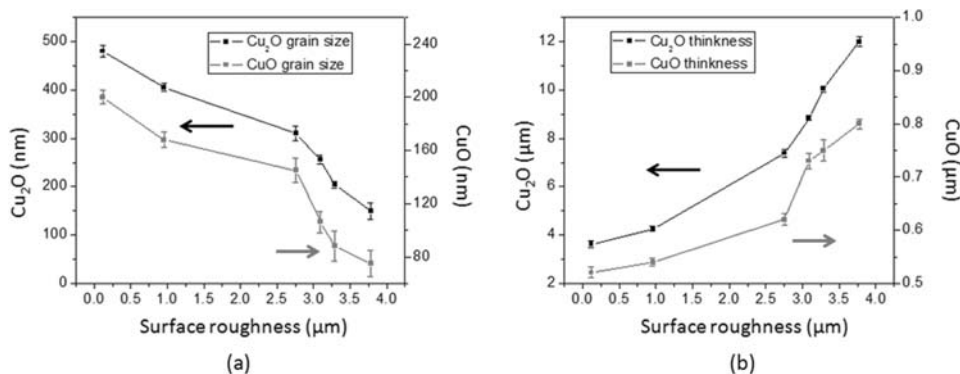
Figure 5. Dependence of the grain size (a) and thickness (b) of Cu_2O and CuO layers on the surface roughness of the Cu substrate sandblasted for different times.

the Cu_2O and CuO layers would greatly influence the formation of CuO nanowires. It has been shown that the growth of oxide scale during the oxidation of Cu is controlled via outward diffusion of cations because of the nature of point defects (i.e., Cu vacancies) in the Cu_2O and CuO layers.[14,15,29–33] CuO nanowire growth requires continuous supply of Cu ions from the substrate (i.e., Cu_2O/Cu interface) to the growth tip. For the intermediate temperatures of the oxidation ($\sim$300 –550°C) for which oxide nanowire formation occurs, the atomic flux sustaining the oxide growth is dominated by grain boundary diffusion of Cu ions across the Cu_2O and CuO layers. A higher density of grain boundaries within the oxide layers leads to more efficient outward diffusion of Cu ions, which not only results in the faster growth of Cu_2O and CuO layers but also enhances the Cu_2O/CuO interfacial reaction that is limited by the bulk diffusion of Cu ions in the Cu_2O layer. The promoted CuO nanowire formation by increasing the surface roughness of the Cu substrates can be understood from the effect of Cu surface roughness on the microstructure characteristics of the Cu_2O and CuO layers, which can be strongly influenced by the behavior of oxide nucleation and growth during the early stages of the oxidation.

The high-temperature oxidation of metals proceeds typically via nucleation, growth and coalescence of oxide nanoislands. For the oxidation of Cu, it first forms Cu_2O nuclei and oxygen surface diffusion is the dominant mechanism for the nucleation of oxide islands.[34–36] The probability of an oxide nucleation event is proportional to the "zones of oxygen capture", and the oxide nuclei density as a function of oxidation time follows the behavior of $N = \frac{1}{L_d^2}(1 - e^{kL_d^2 t})$, where L_d^2 is the area of the zone of oxygen capture, $\frac{1}{L_d^2}$ is the saturation island density, L_d is much larger than the size of the initial nuclei, k is the initial nucleation rate, and t is the oxidation time.[35] The increase in surface roughness by sandblasting can significantly hinder the surface diffusion of oxygen. The restricted oxygn surface mobility gives rise to a smaller capture zone of oxygen, and as a result, leads to a higher density of oxide islands.[37] Therefore, compared to the smooth Cu surface (i.e., the surface without being sandblasted), the oxidation of

sandblasted Cu substrates results in a larger density of Cu_2O islands owing to the increased surface roughness.

Based on our experimental observations and the early-stage oxidation behavior discussed above, the effects of surface roughness on the CuO nanowire formation are schematically shown in Fig. 6. Because of the higher surface density of Cu_2O nuclei for the increased surface roughness by sandblasting, Cu_2O islands impinge while still quite small in their lateral size. Therefore, the fraction of merged grain boundaries is effectively increased and thus conducive to the outward diffusion of Cu ions to support the oxide growth. Since the CuO layer is formed on the Cu_2O layer, smaller Cu_2O grains lead to finer CuO grains and therefore provide more surface sites available for CuO nanowire nucleation to release the interfacial strain generated from the oxide-forming reaction at the CuO/Cu_2O interface. The continued CuO nanowire growth is sustained by the balance between the rates of the strain generation by the Cu_2O/CuO interfacial reaction and the strain relaxation via outward diffusion of Cu cations through the CuO layer. Since the CuO/Cu_2O interfacial reaction is limited by the grain-boundary diffusion of Cu ions across the Cu_2O layer, the increased grain-boundary diffusion enhances the CuO/Cu_2O interfacial reaction. This results in a larger outward flux of Cu ions through the CuO layer, and therefore, a faster growth rate of CuO nanowire. Because the nucleation and growth of CuO nanowires is driven by interfacial strain due to the CuO/Cu_2O interfacial reaction that is controlled by the grain boundary diffusion of Cu ions across the Cu_2O layer, the enhanced nanowire density and growth length is therefore a direct consequence of the enhanced grain boundary diffusion due to the effect of the increased surface roughness of the Cu substrate by sandblasting.

The mechanism described in Fig. 6 stipulates a correspondence of the density and length of CuO nanowires with that of the underlying CuO grains. Our results on the sandblasted Cu substrates indicate that the nanowire density and length increase with increasing the surface roughness. However, our experimental results show no clear dependence of the diameter of CuO nanowires with the Cu surface roughness. This is because the diameter of CuO nanowires is not defined by
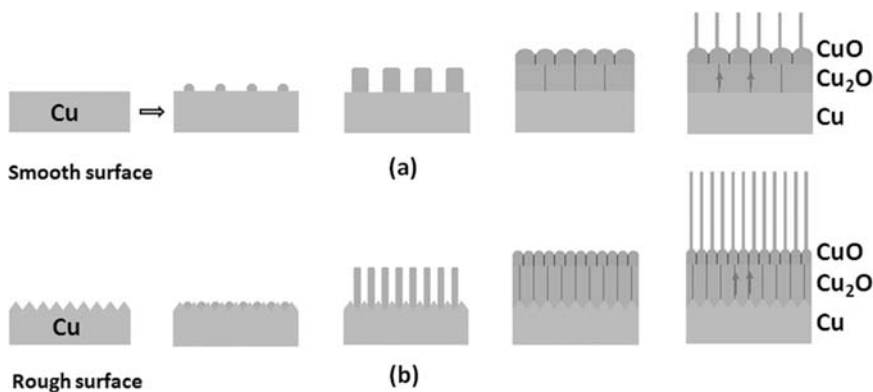

Figure 6. Schematic showing the effect of surface roughness on the microstructure of the oxide layers and the subsequent oxide NW growth, (a) smooth surface; (b) rough surface.

the lateral size of the underlying CuO grains. As revealed by our SEM observations, CuO nanowires are grown from the top portion of CuO grains. Therefore, the diameter of CuO nanowires is typically smaller than the lateral size of underlying CuO grains, leading to the similar range of the diameter distribution of CuO nanowires, irrespective of the different surface roughness of the Cu substrates.

Conclusions

We have studied the effect of surface roughness of Cu substrates modified by sandblasting on the formation of CuO nanowires. The increased surface roughness is observed to promote CuO nanowire formation in terms of both the nucleation density and growth length. Such an enhanced nanowire formation is directly related to the microstructures of the underlying CuO and Cu_2O layers that are strongly influenced by the surface roughness of the Cu substrate. The increased Cu surface roughness restricts the surface mobility of oxygen, which gives rise to a higher nucleation density of Cu_2O islands and therefore increases the fraction of grain boundaries formed by impinged small Cu_2O grains. The efficient outward diffusion of Cu ions via the increased grain boundaries enhances significantly the CuO/Cu_2O interfacial reaction and therefore promotes CuO nanowire formation. This result is expected to have broader impact for understanding of the oxidation mechanisms of metals and also for manipulating the surface oxidation of metals for effectively promoting oxide nanowire formation.

Acknowledgments

References

1. J. G. Lu, P. Chang, and Z. Fan, *Materials Science and Engineering: R: Reports*, **52**, 49 (2006).
2. M. L. Zhong, D. C. Zeng, Z. W. Liu, H. Y. Yu, X. C. Zhong, and W. Q. Qiu, *Acta Materialia*, **58**, 5926 (2010).
3. C. A. N. Fernando, P. H. C. De Silva, S. K. Wethasinha, I. M. Dharmadasa, T. Delsol, and M. C. Simmonds, *Renewable Energy*, **26**, 521 (2002).
4. W. Siripala, A. Ivanovskaya, T. F. Jaramillo, S. H. Baeck, and E. W. McFarland, *Solar Energy Materials and Solar Cells*, **77**, 229 (2003).
5. X. Q. Wang, J. A. Rodriguez, J. C. Hanson, D. Gamarra, A. Martinez-Arias, and M. Fernandez-Garcia, *J. Phys. Chem. B*, **109**, 19595 (2005).
6. X. Q. Wang, J. C. Hanson, A. I. Frenkel, J. Y. Kim, and J. A. Rodriguez, *J. Phys. Chem. B*, **108**, 13667 (2004).
7. P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, and J. Tarascon, *Nature*, **407**, 496 (2000).
8. A. Horne, A. B. Hungria, P. Bera, A. L. Camara, M. Fernandez-Garcia, A. Martinez-Arias, L. Barrio, M. Estrella, G. Zhou, J. J. Fonseca, J. C. Hanson, and J. A. Rodriguez, *Journal of the American Chemical Society*, **132**, 34 (2010).
9. R. Takagi, *J. Phys. Soc. Japan*, **12**, 1212 (1957).
10. Y. W. Park, N. J. Seong, H. J. Jung, A. Chanda, and S. G. Yoon, *Journal of The Electrochemical Society*, **157**, K119 (2010).
11. A. G. Nasibulin, S. Rackauskas, H. Jiang, Y. Tian, P. R. Mudimela, S. D. Shandakov, L. I. Nasibulina, S. Jani, and E. I. Kauppinen, *Nano Research*, **2**, 373 (2010).
12. Y. S. Kim, I. S. Hwang, S. J. Kim, C. Y. Lee, and J. H. Lee, *Sensors and Actuators B: Chemical*, **135**, 298 (2008).
13. G. Garnaud and R. A. Rapp, *Oxidation of Metals*, **11**, 193 (1977).
14. R. A. Rapp, *Metallurgical and Materials Transactions B*, **15**, 195 (1984).
15. K. Mimura, J. W. Lim, M. Isshiki, Y. Zhu, and Q. Jiang, *Metallurgical and Materials Transactions A*, **37**, 1231 (2006).
16. X. Jiang, T. Herricks, and Y. Xia, *Nano Letters*, **2**, 1333 (2002).
17. D. Voss, E. Butler, and T. Mitchell, *Metallurgical and Materials Transactions A*, **13**, 929 (1982).
18. J. T. Chen, F. Zhang, J. Wang, G. A. Zhang, B. B. Miao, X. Y. Fan, D. Yan, and P. X. Yan, *Journal of Alloys and Compounds*, **454**, 268 (2008).
19. L. Yuan, Y. Q. Wang, R. Mema, and G. W. Zhou, *Acta Materialia*, **59**, 2491 (2011).
20. F. Morin, *Journal of materials science letters*, **2**, 383 (1983).
21. R. Mema, L. Yuan, Q. T. Du, Y. Q. Wang, and G. W. Zhou, *Chemical Physics Letters*, **512**, 87 (2011).
22. A. M. Goncalves, L. C. Campos, A. S. Ferlauto, and R. G. Lacerda, *Journal of Applied Physics*, **106**, 034303 (2009).
23. B. J. Hansen, G. H. Lu, and J. H. Chen, *Journal of nanomaterials*, **2008**, 830474 (2008).
24. B. J. Hansen, H. I. Chan, J. Lu, G. H. Lu, and J. H. Chen, *Chemical Physics Letters*, **504**, 41 (2011).
25. G. Honjo, *Journal of the Physical Society of Japan*, **4**, 330 (1949).
26. Y. Zhu, K. Mimura, and M. Isshiki, *Corrosion Science*, **46**, 2445 (2004).
27. Y. Zhu, K. Mimura, S.-H. Hong, and M. Isshiki, *Journal of The Electrochemical Society*, **152**, B296 (2005).
28. Y. Zhu, K. Mimura, and M. Isshiki, *Corrosion Science*, **47**, 537 (2005).
29. G. Raynaud and R. Rapp, *Oxidation of Metals*, **21**, 89 (1984).
30. H. Evans, *International materials reviews*, **40**, 1 (1995).
31. Y. Zhu, K. Mimura, and M. Isshiki, *Materials transactions*, **43**, 2173 (2002).
32. Y. Zhu, K. Mimura, and M. Isshiki, *Oxidation of Metals*, **62**, 207 (2004).
33. Z. Grzesik and M. Migdalska, *Defect and Diffusion Forum*, **289**, 429 (2009).
34. J. C. Yang, B. Kolasa, and J. M. Gibson, *Applied Physics Letters*, **70**, 3522 (1997).
35. J. C. Yang, M. Yeadon, B. Kolasa, and J. M. Gibson, *Scripta Materialia*, **38**, 1237 (1998).
36. G. W. Zhou and J. C. Yang, *Surface Science*, **531**, 359 (2003).
37. G. W. Zhou and J. C. Yang, *Surface Science*, **559**, 100 (2004).