Vapor-quasiliquid-solid (VQS) mechanismof one-dimensional nanostructure growth based Cu catalyst

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Abstract: The submicron-rods of Cu_2O with diameters of 100-700 nm and lengths of 2-8 μm were synthesized by radio frequency magnetron sputtering. The abundance of Cu species, which is modulated by the Ar/O_2 ratio during the sputtering process affect directly to the growths of the Cu_2O branches on the bodies of the submicron-rods. Transmission electron microscopy and elemental mapping reveal that metallic Cu are existed on the heads of the Cu_2O rods. The growth rate, catalyst phase and shape reveal that vapor-quasiliquid-solid was the growth mechanism of the formations of those structures.

1. Introduction

It is well known that vapor-liquid-solid (VLS) and vapor-solid-solid (VSS) are frequently assigned as catalyst-based growth mechanism of nanorods/nanowires[1,2]. Recently, it is found that VSS mechanism is actually vapor-quasisolid-solid (VQS) mechanism because solid diffusion during the VSS mechanism can yield only very low growth rate (just fraction of a nanometer per second)[3]. Growth of one-dimensional nanostructure based Cu catalyst is a very interesting issue that has not been studied previously. As Cu is the catalyst, the issue is how the growth processes because the melting temperature of bulk Cu is 1084 ^oC which is a elevated growth temperature.

Cuprous oxide (Cu_2O) is a potential p-type metal-oxide semiconductor with a direct bandgap of ~2.17 eV. With excellent optical and magnetic properties, Cu_2O has been applied in many fields, Although Cu_2O thin films deposited by sputtering were extensively studied[4-6], rod-like structure of Cu_2O on MgO(011) thin film deposited by DC facing-magnetron sputtering was firstly observed by Yin et al.[7], to the best of our knowledge. Nevertheless, detail study about the growth process of Cu_2O rod-like structure via sputtering route is still lack of concern.

In this paper, Cu_2O submicron-sized rods and trees were grown on glass substrate under metal-mode condition by RF magnetron sputtering. The VQS mechanism based Cu catalyst of the structures was carefully described.

2. Main results

Elemental mapping and line-scan analyses were carried out for the submicron-tree sample to reveal the element behind the ellipsoidally shaped particle. As expected, a Cu particle was found at the rod head, as follows from the data shown in figure 7(d-e). In addition, Cu seeds are also formulated on the body of the Cu_2O rod as in figure 7(a-c). As Cu is the catalyst, the issue is how the growth processes because the melting temperature of bulk Cu is 1084 ^oC which is much higher than our sputtering temperature. It is different with the bulk, the nanoscale of metallic Cu can be melted at much lower temperature. Study of Oleg A. Yeshchenko et al. in the temperature dependences of the bandwidth and energy of surface plasmon in spherical Cu nanoparticles embedded in silica matrix indicated that the temperature of melting of the Cu nanoparticle with diameter $\leq$ 43 nm was below 550 ^oC[8]. This melting point (T = 550 ^oC) was similar to the surface melting temperature of the Cu nanoparticles with diameter of 45 nm. In another study, Sung-Hyeon Park et al. found that the average melting temperature of the commercially available copper nanoparticles with oxide shells (10-70 nm in diameter, oxide thickness >2 nm) was approximately 274 ^oC[9]. Therefore, phase of the Cu nuclei with diameters of below 100 nm appeared on the head and body of the rod (figure 1(a, d)) were possibly liquid during the sputtering at elevated temperature (T $\geq$ 400 ^oC). Besides, it is well known that the equilibrium shape of a liquid in a uniform force field is spherical shape[10] which was found as the shape of Cu nuclei in figure 1(a-c).

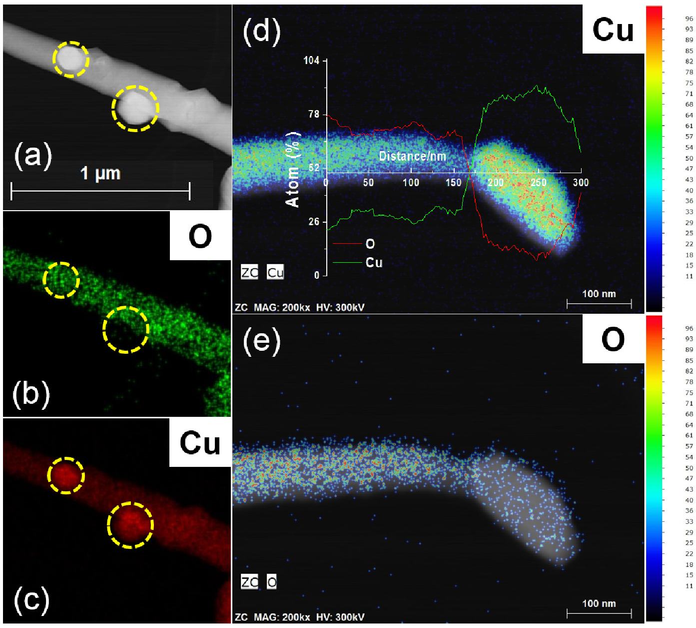

Fig. 1. Elemental mapping images of the branch body (a–c); Elemental mapping images and line scan analysis of the branch head (d, e).

It is known that the growth kinetics of the thin-film microstructure produced by sputtering depends mainly on 4 factors: substrate temperature, topography of the substrate, gaseous environment, and source/energy of impurity/catalyst species. Here, the catalyst species were generated in-situ by modulating the oxygen partial pressure during the synthesis which resulted in the formations of Cu_2O submicron-rods and submicron-trees.

The quantity of Cu species available during the sputtering process does not only determine the shapes of the Cu_2O rods, but also leads to a new morphology of submicron-sized Cu_2O trees. By reducing the amount of oxygen (Ar/O_2 = 97/3), more Cu species are generated in the sputtering chamber, meaning that a larger number of Cu_2O submicron rods are consequently synthesized. The Cu_2O thin film is subsequently covered by a large number of Cu_2O submicron rods. Therefore, newly incident particles are mainly adsorbed at the rod bodies rather than at the underlying film. The growth of Cu_2O rods beneath secondary nuclei was progressed by the incoming Cu_2O species. New nuclei can also be created on secondary rods that, in turn, may build up new rods. Finally, tree-like submicron-sized structures of Cu_2O were synthesized.

3. Conclusions

In conclusion, cuprous oxide submicron-sized rods (large head/small root with diameters of 100–700 nm and lengths of 2–8 μm), and submicron trees were grown on thin films of Cu_2O at 550 °C corresponding to Opp = 5 % and 3 % by RF-magnetron sputtering. The formation mechanism of the Cu_2O submicron-sized rods and trees was confirmed to be grown by VQS mechanism. Metallic Cu was found to act as a catalyst during the growth. The decrease of oxygen partial pressure during the sputtering resulted in a larger amount of Cu species which then affected directly to the growth behavior of the Cu_2O morphologies. These results may be expanded to tailor the morphologies of other metal oxide materials using sputtering system.

References

1. Schmidt V, Wittemann JV, Senz S, Gösele U. Adv. Mater. 2009;21:2681.
2. Wang Y, Schmidt V, Senz S, Gösele U. Nat. Nanotechnol. 2006;1:186.
3. Mohammad SN. J. Chem. Phys. 2009;131:224702.
4. Yin ZG, Zhang HT, Goodner DM, Bedzyk MJ, et al. Appl Phys Lett 2005;86:061901.
5. Reddya AS, Uthannab S, Reddy PS. Appl Surf Sci 2007;253:5287.
6. Zhu H, Zhang J, Li C, Pan F, Wang T, Huang B. Thin Solid Films 2009;517:5700.
7. Liao L, Zhang Q, Su Z, Zhao Z, Wang Y, Li Y, et al. Nat Nanotechnol 2014;9:69.
8. Yeshchenko OA, Dmitruk IM, Alexeenko AA, Dmytruk AM. Phys. Rev. B: Condens. Matter 2007;75:085434.
9. Park SH, Chunga WH, Kim HS. J. Mater. Process. Technol. 2014;214:2730.
10. Liao Q, Shi Y, Fan Y, Zhu X, Wang H. Appl. Therm. Eng. 2009;29:372.