The effect of vapor concentration on the formation of nanowires

Yongjun Chen¹, Jianbao Li², Yongsheng Han², Jinhui Dai², Xiaozhan Yang², Ying Chen¹

¹Department of Electronic Materials Engineering, Research School of Physical Science and Engineering, Australian National University, ACT, 0200, Canberra, Australia
²Department of Materials Science & Engineering, State Key Laboratory of New Ceramics & Fine Processing, Tsinghua University, 100084, Beijing, China
E-mail of corresponding author: yong.chen@anu.edu.au

Introduction

Generally, in both chemical vapor deposition (CVD) and physical vapor deposition (PVD) process, the vapor supersaturation degree in reaction chamber could significantly affect the morphology of nanowires. Blocher [1] depicted the effects of deposition temperature and relative vapor supersaturation degrees on the product morphology in detail: with the increase of deposition temperature and decrease of supersaturation degree, the product transforms from amorphous phase to single crystalline phase, and the morphology changes from particle shape to fiber, film and finally three dimensional crystals. It was also found that, at a certain deposition temperature, morphology and growth mechanism of nanowires could be affected by supersaturation degree (vapor concentration) in the chamber significantly [2-4]. When preparing magnesium oxide (MgO) nanostructures [5], we obtained MgO nanowires and nanoribbons at a relatively low Mg vapor concentration, which grew via vapor-liquid-solid (VLS) and vapor-solid (VS) mechanism, respectively; at a relatively high Mg vapor concentration, MgO microsized whiskers or crystal ribbons formed via VS mechanism. In the case of preparation of Si and SiOₓ (x=1-2) nanowires [6], when Si vapor concentration is high, Si nanowires formed via an oxide assisted (OA) model; when SiOₓ vapor concentration is high, SiOₓ nanowires and Si nanorods formed via VS and VLS mechanisms, respectively.

Experimental procedure

MgO nanowires:
MgO nanowires were prepared using two different starting materials to generate Mg vapor:
1) A mixture of activated carbon and MgO powders. The mixture was placed in an Al₂O₃ boat, which was placed at the center of a tube. A Mg+B+Si (molar ratio of Mg:B:Si = 2:1:0.02, Si was added as catalyst) pellet was placed in another Al₂O₃ boat that was placed near the first boat with a distance of 10 mm in a downstream direction. After flushing with pure Ar gas to eliminate the residual air, the furnace was heated to 1250°C and held for 1 hour, then cooled down to room temperature.
2) Pure Mg powder. The Mg boat was moved toward the inlet direction of the tube for 10 mm and the pellet was placed at the center of the tube. The reaction temperature was also changed to 950°C, so that the location temperature of the pellets is same in both cases. After the annealing, a thin white-grey layer formed on the surface of the pellets. Particularly, at the edge of the pellet in case 2, a small white fluffy lump formed.

Si and SiOₓ nanowires:
The experimental setup is the same as that described above. Pure Si powder was used as Si vapor source and a catalyst (Fe)-coated quartz strip was used as substrate. The reaction temperature and holding time were 1100°C and 30 min, respectively. After experiment, it was found that a thin layer of brown deposition formed on the substrate.

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All deposition samples were characterized using field emission scanning electron microscopy (FE-SEM, JSM-6301F), transmission electron microscopy (TEM, JEM-200CX, 200 kv), high-resolution transmission electron microscopy (HRTEM, JEM-2010F, 200 kv). The chemical compositions were identified with X-ray diffraction (XRD) (nickel-filtered CuKα radiation) and X-ray energy dispersive spectrometer (EDS) attached to SEM and HETEM (Link ISIS-300), respectively.

**Results**

*MgO nanowires*

XRD and EDS results indicate that the white-gray and lump substances formed from the MgO-C mixture are composed of MgO phase. The SEM image in Fig.1a shows MgO nanowires with a diameter between 30-80 nm and a length of several to tens of micrometers. The high magnification image (inset Fig. 1a) displays a small irregular SiO₂ particle (determined by EDS) attached at the end of some nanowires. The SEM image in Fig.1b reveals that some MgO nanoribbons with width of about 700 nm and thickness of 60-80 nm also formed. Small particles are not found at their ends.

![MgO nanowires and nanoribbons](image1)

The SEM image in Fig.1c shows the white deposition formed at the edge of the pellet 2 from Mg powder consists of dense and long micro-sized MgO whiskers with a length up to hundreds of micrometers. High magnification image (inset Fig.1c) reveals that they exhibit a pillar shape with a rectangular cross-section, and the diameter is about 600 nm, which is larger than that of the nanowires formed on pellet 1. Micro-sized MgO ribbons also formed (Fig.1d) with a width of 2.4 µm and thickness of 1.5 µm (the inset image clearly shows the size).

*Presenting author’s name: Y.J. Chen*
Si and SiOx nanowires

Fig. 2a illustrates the zone distribution of with high and low temperature of the substrate. The SEM image in Fig. 2b shows Si and SiOx nanowires formed in the high-temperature zone (near Si source) have diameters of 40–250 nm and a length of tens to hundreds of micrometer. The inset image shows that most nanowires have a fist-like particle attached at the end. In the low-temperature zone, a structure consists of short Si rod and a long SiOx (EDS reveals that x=1–2) nanowire-bundle formed, which were shown in Fig. 2c. EDS indicates that there is a small plate-like Fe particle at the end of Si rod.

Discussion

In the case of MgO nanowires, Si powders were added in the pellets as catalyst. Si and Mg can form a liquid Mg-Si alloy because the reaction temperature is higher than the eutectic point of Mg-Si alloy (637.6°C) [7]. Thus the nanowires should grow out via a VLS mechanism. However, different Mg vapor sources generated different Mg vapor concentrations, and eventually produced different nanowire sizes and growth mechanisms. The concentration of Mg vapor generated by carbothermal reduction is low but much more stable than those generated by directly heating Mg powder. In the case of MgO+C, the slowly and stably generated Mg vapor will dissolve in liquid Mg-Si alloy droplet, and after the liquid become supersaturated, Mg crystal nucleates and MgO nanowires start to grow. The nanowire growth continues as long as the catalyst alloy remains in a liquid state and Mg vapor is available. The whole process is a typical VLS process. Because Mg can be oxidized much more easily, the product is MgO instead of Mg nanowires. At the same time, the smaller is the droplet size and the lower the Mg vapor concentration, the smaller is the diameter of nanowires and nanoribbons formed. In the case of Mg, liquid Mg-Si alloy droplets also formed, but because Mg vapor concentration is too high, the droplets can only consume a
small amount of Mg vapor, and most Mg vapor will deposit on the surface of the grown whiskers and ribbons, making the whiskers and ribbons lengthen and thicken, then micro-sized whiskers and ribbons formed via a VS process.

In the case of Si-SiOx nanowires, the competitive growth between Si and SiOx nanowires caused by the concentration differences between Si vapor and SiOx vapor resulted in different nanowire composition and growth mechanisms. SiOx vapor is probably generated by Si vapor reacting with quartz substrate at high temperature. When the concentration of Si vapor is very high and the concentration of SiOx vapor is very low, because the SiOx vapor generated in this zone may be mainly taken away by Ar flow, thick and long Si nanowires formed via an oxide-assisted (OA) model, which is similar to the work of Zhang et al. [8]. In low-temperature zone, however, the Si vapor concentration is very low while SiOx vapor concentration is very high. Therefore, the final structure consists of long SiOx nanowires with a short Si nanorod formed via VS and VLS process, respectively.

Conclusion

In CVD process, the vapor concentration affects the nanowire size and growth mechanism significantly. We found that low concentration Mg vapor favors the formation of MgO nanowires and nanoribbons, which grew via VLS and VS mechanism, respectively; while high concentration Mg vapor produces large micro-sized MgO whiskers and ribbons via VS mechanism. High concentration Si vapor favors the formation of long and thick Si nanowires that grew via oxide assisted model, while high concentration SiOx vapor produces the long and thin SiOx nanowires via a VS mechanism and short Si nanorods via a VLS process.

References


Presenting author’s name: Y.J. Chen