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Effects of supply time of Ar gas current on structural properties of Au-catalyzed ZnO nanowires on silicon (1 0 0) grown by vapor–liquid–solid process

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Abstract

ZnO nanowires were grown on Au-coated Si (1 0 0) substrates by the method of vapor–liquid–solid (VLS) growth processing technique. The effects of supply time of Ar gas current on morphology and microstructure of Au-catalyzed ZnO nanowires were investigated by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) and Raman spectroscopy. The results showed that the morphologies of ZnO nanostructures strongly depended on the time of flowing Ar gas. When the time of flowing Ar gas was 90 s, ZnO showed nanowires with hexagonal structure. Their diameters and lengths were 160 nm and 20 μm, respectively, on average, and the Raman scattering peak located at 438 cm^{-1} reached maximum intensity. The results also showed that the ZnO growth could be patterned by controlling the initial position of Au-coated area on the Si substrates.

Keywords: ZnO nanowires; Vapor–liquid–solid (VLS); Raman spectroscopy

1. Introduction

On one hand, one-dimensional nanostructures, such as wires, rods, belts and tubes have become the focus of intensive research owing to their unique applications in mesoscopic physics and fabrication of nanoscaled devices [1]. On the other hand, Zinc oxide (ZnO) as a wide band gap semiconductor attracts a lot of intention in current semiconductor research, due to a number of advantages it presents in comparison with GaN, such as the larger exciton binding energy, availability of large area substrates for homo-epitaxy, etc. [2]. ZnO nanowires have the high mechanical stability, high aspect ratio and negative electron affinity in various vacuum environments. They are promising to be an excellent nanomaterial for their tunable electronic and optoelectronic properties, and the potential applications in the nanoscale electronic and optoelectronic devices [3–5]. Recently, considerable efforts have been made to investigate ZnO nanowires in respect of theory and experiment. High-quality ZnO nanowires and thin films have been mainly grown on sapphire substrates [6–13] by metal organic chemical vapor deposition (MOCVD) and metal organic vapor phase epitaxy (MOVPE). These methods involve complex procedures and sophisticated equipment. Moreover, the sapphire substrates are rare, expensive and difficult to integrate. In this paper, using Si (0 0 1) as the substrate we investigated systematically the effects of flowing time of Ar on structural properties of nanocrystalline zinc oxide by the vapor–liquid–solid (VLS) technique. The method is suitable for large wafer size growth, and the growth process is relatively simple. It was found that the formation and orientation of ZnO nanostructures were strongly influenced by the growth conditions, such as gas-supply time and gas composition.

2. Experimental

In this work, the Si substrate was cleaned firstly in an ultrasonic bath with absolute alcohol and acetone for 15 min at room temperature, respectively, and

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then washed using de-ionized firstly water. The Au layer was deposited on the cleaned Si (1 0 0) substrate by rf-sputtering.

ZnO (99.99%, 325 mesh, Alfa Aesar) and carbon (99.99%, 325 mesh, Alfa Aesar) powders were mixed with equal weight. Then the mixture was placed in an alumina boat, and the Si substrate coated with Au was laid on the edge of the alumina boat, which is just above the material sources. At last, the alumina boat was placed into a small quartz tube avoiding the pollution. Then the small quartz tube was placed inside a horizontal tube furnace. The initial temperature of the furnace was 850 °C. With the Ar gas flowing into the furnace, the temperature of the furnace was synchronously ramped to 900 °C rapidly. Then the furnace was kept at the temperature of 900 °C for 1 h. After the furnace was cooled to room temperature, light or dark gray film was found on the substrates. The process is slight different from the catalyst growth, which is referred to the vapor phase transport process [6]. In this experiment, Si substrates are above the mixture but not downstream, so the Ar gas does not act as transportation gas but adjust the ambient gas composition in the furnace. Five samples denoted as (a–e) were synthesized with different supply time of the Ar gas current, which correspond to 10, 30, 90, 180 and 600 s, respectively. When the supply time of Ar gas current was 90 s, ZnO nanowire spots (denoted as f) were also formed by patterning the Au film on the Si substrate.

XRD (MAC Science, MXP18, Japan), SEM (Hitachi, S-570) and Raman (LABRAM-UV, Jobin Yvon, France) were used to characterize the crystal structure, surface morphology of the ZnO nanowires.

3. Results and discussion

Fig. 1 shows the XRD patterns of the ZnO synthesized with different supply time of Ar gas current. It can be seen that all the diffraction peaks observed from Fig. 1 could be identified to ZnO peaks compared with the standard card of bulk ZnO with hexagonal structure (JCPDS No. 800075). And there were no diffraction peaks of other impurities, which indicated all the samples were single phase of ZnO. In addition, it also can be seen that the crystal orientation and quality are strongly dependent on the supply time of Ar gas current. Fig. 1a–c shows that the intensity of the peak (0 0 2) is significantly enhanced by increasing supply time of Ar gas current from 10 to 90 s, which shows that the growth orientation of ZnO nanocrystals is mostly random at the initial stage, but becomes well oriented along (0 0 2) direction. The strong and sharp (0 0 2) peak indicates the ZnO nanowires exhibit a preferred (0 0 2) orientation. The sample c shows that the best oriented growth for the time of flowing Ar gas is regulated to 90 s. With increasing different supply time of Ar gas current from 180 to 600 s, the (0 0 2) peak declined greatly and the peak disappeared when the time increased to 600 s (Fig. 1d).

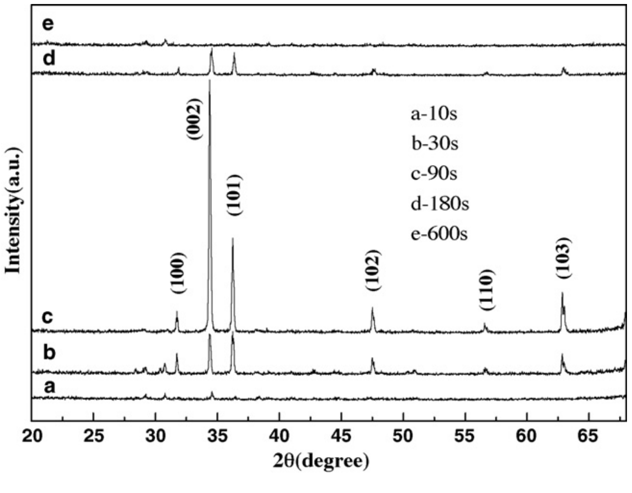

Fig. 1. XRD patterns of ZnO nanowires synthesized with different supply time of Ar gas current.

In our studies, ZnO growth is attributed to the VLS crystal growth mechanism. In this process, the super saturation of alloy droplet plays an important role in the nucleation and growth process. When Zn in the alloy droplet is supersaturated, new phase forms. Zinc oxide has the higher melting point, so ZnO is reduced by graphite firstly (at 900 °C) to form Zn, and Zn (melting temperature is about 419 °C) in the vapor phase is condensed to form liquid droplets on Si substrate as nuclear for ZnO nanowire growth. Then Zn in the liquid droplets is oxidized. Enhanced absorption and diffusion of ZnO occurred at the liquid tips. Eventually, ZnO super saturation results in ZnO segregation and nanowires array growth. But it is also believed that the content of oxygen in the system may be another important factor in the process. In our studies, Si substrate was above the mixture, so the Ar gas did not act as transport gas but used to change the composition in the system. If the supply time of the Ar gas current was too long (180, 600 s) or too short (10, 30 s), the content of the oxygen was lower or higher in the system. It means that there is a critical content of oxygen for redox. Therefore, different ZnO nanostructures were formed with the different supply time of the Ar gas in our experiments.

Fig. 2a–e shows the scanning electron microscopy (SEM) images of the samples with different supply time of Ar gas current, which ranges from 10 to 600 s. Fig. 2f shows the SEM image of the ZnO sample grown on the patterned Au film. When the time is 10 or 30 s, the sample shows chips and wires. The chips are quadrate or triquetrous. The thickness is about 20 nm, and the surfaces are smooth. It can also be seen that some nanowires grow on the chips. The length and diameter of these nanowires are changed from 15 μm to 120 nm. When the time is 90 s, the products are all nanowires (Fig. 2c). The angle between nanowires and substrate plane are at the range of 45–80°. The diameter of these ZnO nanowires varies from 50 to 250 nm, and the average of it is around 160 nm. The average ratio of length/diameter of the ZnO nanowires is estimated larger than 13. The inset image is the magnified view of single nanowire. It can be seen clearly that the tip of nanowire is hexagonal. When the supply time increased to 180 s, big chips appeared again. Moreover, there is only something like island on the surface of the substrate when the supply time is 600 s. It is believed that these islands are alloys of ZnO and Au. That is to say, there are no nanowires formed on the substrate when the supply time of Ar gas current is too long, which can also be testified by Fig. 1e. According to Fig. 2f, there are four white spots and the distance between them is equal, which is because the substrate of f sample was coated with equidistant Au cluster and the distance between them is about 2 mm. So it is can be believed that the positions of the nanowires can be controlled by the initial position of Au film patterns. The inset in Fig. 2f is the magnified images of the spot. It can be seen from it that there are many nanowires in the spots.

Raman scattering is very sensitive to the microstructure of nanosized materials. It is used here to clarify the structure of

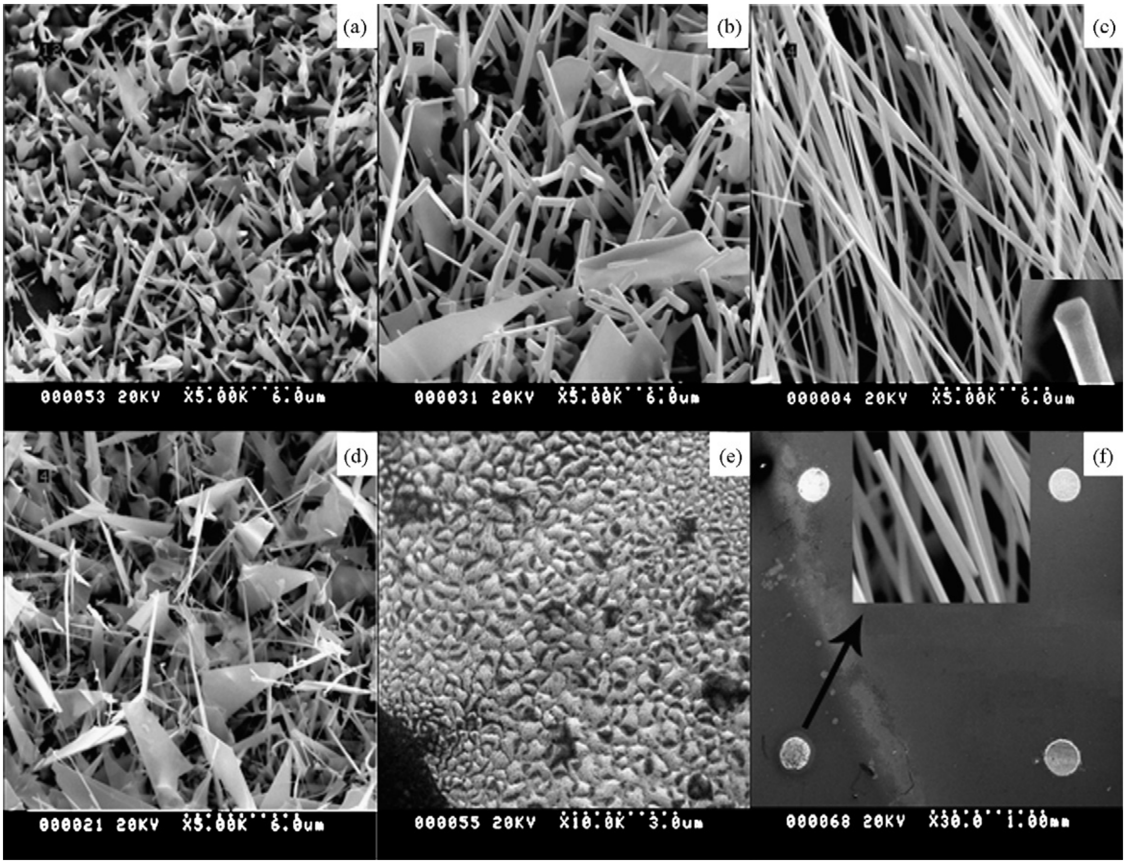

Fig. 2. SEM images of ZnO nanostructure grown with different supply time of Ar gas current: (a) 10 s, (b) 30 s, (c) 90 s and the inset in c is its magnified view, (d) 180 s, (e) 600 s and (f) 90 s, sample which produced with patterning Au particles and the inset in f is its magnified view of ZnO spots.

ZnO nanowires. Wurtzite-type ZnO belongs to the space group C_{6v}^{4} with two formula units in the primitive cell. The optical phonons at Γ point of the Brillouin zone belong to the following irreducible representation: $\Gamma_{\text{opt}} = 1A_1 + 2B_1 + 1E_1 + 1E_1 + 2E_2$. Both A_1 and E_1 modes are polar and split into transverse (TO) and longitudinal optical (LO) phonons, all being Raman and infrared active [14]. The two nonpolar E_2 modes ($E_2^{(1)}$, $E_2^{(2)}$) are Raman active only. The B_1 modes are infrared and Raman inactive (silent modes). Fig. 3a–c showed the Raman spectra for three samples. The peaks located at 304, 521 and 620 cm^{-1} are Si vibration modes. The peaks located at 330, 380, 438 and 578 cm^{-1} are assigned to second-order Raman spectrum $2E_2$ (M), A_{1T}, E_{2H} and E_{1L}, respectively. The E_{2H} mode involving only oxygen atoms articulates that the nanowires are of high-quality crystal [15]. The E_{1L} mode associated with oxygen deficiency indicated that oxygen vacancies existed in the nanowires [16]. Therefore, according to Fig. 3c, the strong peak dominating at 438.69 cm^{-1} and the absence of the E_{1L} mode at 578 cm^{-1} indicated that the as-grown products (sample c) are excellent single crystal with hexagonal wurtzite structure and low level of oxygen vacancies.

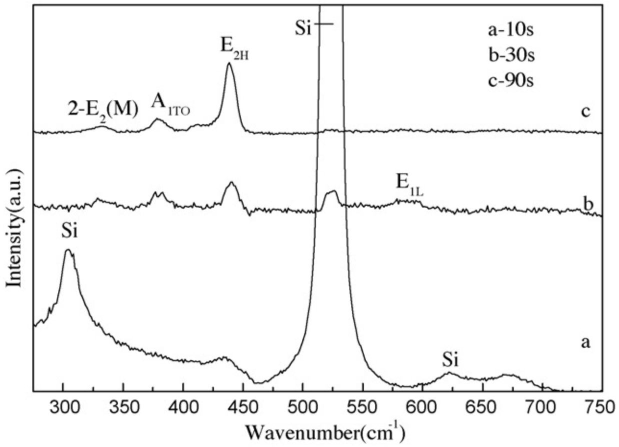

Fig. 3. Room temperature Raman spectra of ZnO nanowires synthesized with different supply time of Ar gas.

4. Conclusions

The orientated ZnO nanowires were successfully grown on Si substrates by VLS method. The results showed that the formation and position of ZnO nanostructures strongly depended on the growth conditions. When the supply time of Ar gas current was 90 s, the orientated ZnO nanowires with diameter of around 160 nm and length of 20 μm have been fabricated.

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