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ZnO hexagonal prisms grown onto p-Si (1 1 1) substrate from poly (vinylpyrrolidone) assisted electrochemical assembly

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Abstract

Nonionic polymer poly (vinylpyrrolidone) (PVP) was firstly mixed into oxygenated zinc chloride electrolyte to modulate the crystal growth and morphology of ZnO from electrodeposition. Arrays of ZnO hexagonal prisms with well-defined (0 0 0 1) end facets and {1 0 $\bar{1}$ 0} side facets were grown perpendicularly onto p-type Si substrates using the simple and economic route. It was observed that the concentration of PVP played an important role in the final morphology and size of ZnO crystals. The optical studies indicated that the addition of PVT not only influenced crystal growth habit but also improved the optical properties of ZnO.
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1. Introduction

ZnO as a wide band gap II–VI semiconductor has been extensively investigated due to its wide application in optical waveguides, transparent conducting coatings and short wavelength optical devices. The morphology, size, orientation and even crystal density are of significant importance for the applications of this material. ZnO crystals with various shapes such as nanorods [1–9], nanowires [10–12], nanobelts [13–15], mesoporous [16] and helical [17] structures have been synthesized using a variety of technologies. Among these, ordered, aligned ZnO hexagonal nanorods are of particular interest due to their significance in both scientific research and technological application [4–9]. Especially, the well-faced nature of these prisms with two naturally faceted ends provides a well-defined resonance cavity for stimulated emission,

which is significant for the realization of laser action [18]. Common methods of growing oriented nanomaterials arrays include vapor transfer [10,19–21], metalorganic vapor-phase epitaxial growth [2,9,22], application of a physical template [23,24], and hydrothermal solution synthesis [5,6]. Polymers have been widely employed in chemical routes to control the nucleation, growth and alignment of inorganic crystals [8,25–30], while the use of polymers in electrodeposition to produce ordered ZnO arrays has rarely been reported. Choi et al. [31] recently reported that potential controlled surfactant assembled at the solid–liquid interface as templates for the production of ZnO nanostructure from electrodeposition. Yoshida et al. [32] described electrochemical self-assembly of dye-modified ZnO films with addition of dye molecules into the deposition bath. Dye addition not only affected the growth of ZnO but also resulted in incorporation of dye molecules into ZnO films, which can be applied in dye-sensitized solar cells [32–34].

In this paper, a simple and low-temperature electrochemical method was described to grow highly oriented

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arrays of ZnO hexagonal prisms onto p-type Si substrates. Our strategy is using electrochemical process to control the nucleation of ZnO and poly(vinylpyrrolidone) (PVP) mixed into the electrolyte to modulate the growth of ZnO. It has been reported that ZnO prisms with hexagonal faces can be directly electrodeposited from O_2 saturated zinc chloride aqueous solution [35–37]. However, these prisms were short in length, and were overlapping, making them difficult to use in practical applications [35]. Polymers are known to have different interaction strengths with different facets of inorganic crystals, which can selectively promote or inhibit the growth of certain facets, allowing fabrication of complex forms [8,29,30]. The experimental results reveal that PVP can effectively promote vertical growth while inhibit lateral growth of ZnO crystals. This technology is conducted at low temperature and does not require complicated procedures or a support template. Another unique advantage of this method is that the fabricated film is pure with no unwanted byproducts. This is because that the polymers adsorbed on the surfaces of inorganic crystals can be totally washed away with deionized water or ethanol [31].

2. Experimental procedure

Using a method similar to that developed by Peulon and Lincot [38,39], the experiment was carried out potentiostatically at –0.6 V (vs Ag/AgCl reference electrode) for 1 h, in an O_2 saturated aqueous solution containing 0.005 M $ZnCl_2$ and 0.1 M KCl maintained at 60 °C. In the PVP-assisted growth experiments, various weight percents of PVP were added into the electrolyte and the mixed solutions were stirred by a magnetic stirring to dissolve PVP thoroughly. The substrates were p-type, [1 1 1] oriented Si wafers. Before electrodeposition the Si substrates were sequentially ultrasonically cleaned in acetone, ethanol, and water, 10 min each and then immersed in a 5% HF solution for oxide removal, followed by rinsing with deionized water. Following deposition, the samples were removed from the electrochemical cell and rinsed with ethanol and deionized water.

The morphologies of the samples were investigated using a Hitachi S4200 field-emission scanning electron microscope. X-ray diffraction (XRD) spectra were measured using a rotating anode X-ray diffractometer with Cu Kα1 radiation of 1.541 Å. Film reflectance spectra were measured using a Hitachi MPF-4 spectrophotometer. The room temperature-photoluminescence (PL) spectra of the films were obtained with a UV Labran Infinity Spectrophotometer made by J–Y Company, which is excited by the 325 nm line of a He–Cd laser.

3. Results and discussion

The plain-view SEM image of ZnO grown from PVP-free solution is shown in Fig. 1(a). Densely packed ZnO crystals fully cover the Si substrate. The width of the
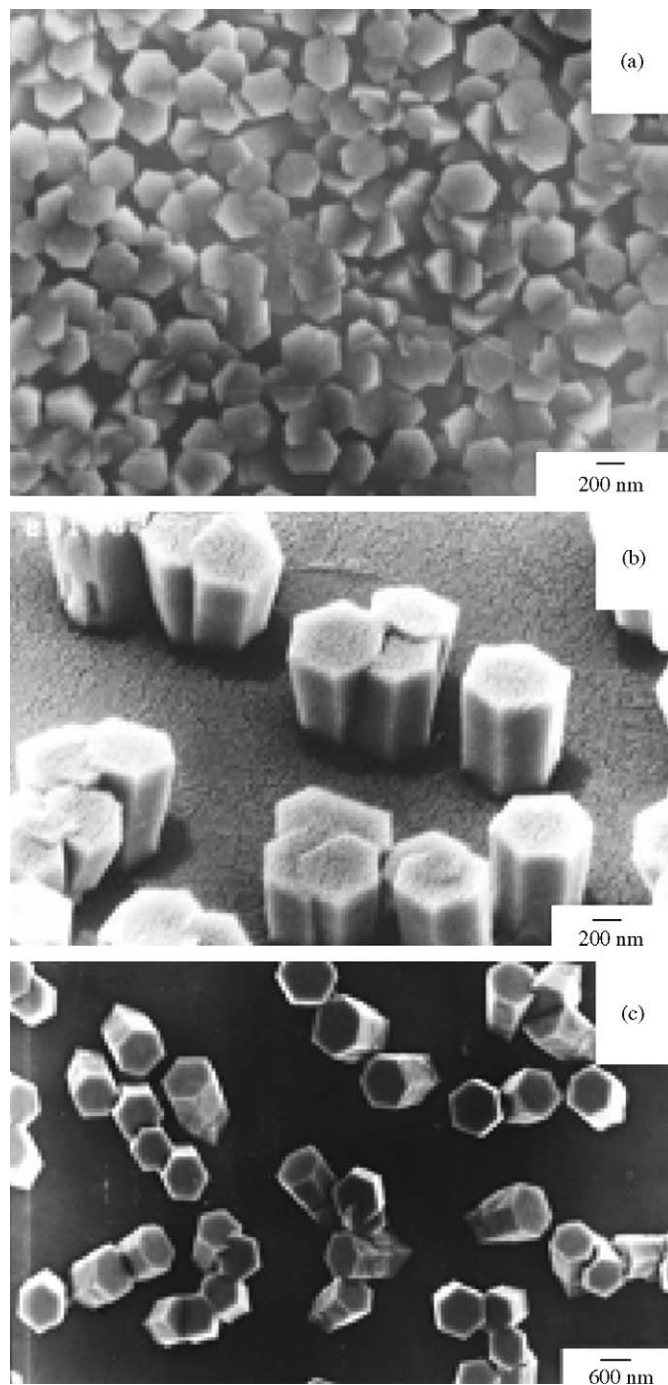

Fig. 1. The field-emission SEM photographs of the ZnO films grown from deposition bath containing (a) no PVP; (b) 0.1 wt% PVP; and (c) 0.5 wt% PVP; (b) is the tiled-view photograph.

hexagonal faces is about 150 nm and the height of the prisms is no longer than 200 nm, as calculated from the cross-sectional view. Interestingly, obvious differences can be observed from the SEM images for the samples grown from PVP-containing solutions. The low-magnification SEM image of the sample (not shown) grown in the presence of 0.1 wt% PVP shows significantly reduced surface coverage of ZnO on the Si substrate, and the

hexagonal crystals are partly separated. The tilted view of this sample given in Fig. 1(b) shows straight, smooth, and uniform ZnO hexagonal prisms grown perpendicularly on the substrate with clearly identifiable (0 0 0 1) end facets and the {1 0 $\bar{1}$ 0} side facets. The width of the hexagonal ends is about 250 nm, and the height of the prisms is approximately 500 nm. In this sample, growth of [0 0 0 1] orientation of ZnO columns is obviously enhanced. Although some ZnO prisms are still aggregated and overlapping, some have been separated from the clusters. Further separated and longer ZnO hexagonal prisms were observed when PVP concentration is increased to 0.5 wt%. Fig. 1(c) shows the SEM photograph of ZnO films grown from an bath solution containing 0.5 wt% PVP. Arrays of well-separated ZnO hexagonal prisms are fabricated on Si substrate. The height of these prisms is about 1 μm. Such separated and aligned hexagonal structures on Si substrate provide potential application in many fields such as molecular electronics or data storage. From the SEM photographs, it is observed that addition of PVP into the deposition bath can effectively separates ZnO columns and selectively enhanced growth in the [0 0 0 1] orientation.

The crystal structure and preferential orientation of the ZnO crystals were further investigated by measuring the XRD patterns. As shown in Fig. 2, all the samples show 0 0 0 2 dominated diffraction peak, indicating an accordant c-axis crystallographic orientation of these samples. It is observed that the 0 0 0 2 diffraction peak of the sample grown from 0.1 wt% PVP solution increased significantly compared to the sample grown from PVP-free solution. The enhanced intensity of the 0 0 0 2 diffraction peak is consistent with the SEM results, which indicates that the sample is highly [0 0 0 1] oriented. One thing should be mentioned that although the sample grown with 0.5 wt%

PVP grows more quickly in the c-axis orientation observed from the SEM, the intensity of the 0 0 0 2 peak in the XRD pattern decreased compared to that of the sample grown from 0.1 wt% PVP solution. This is caused by the decreased surface coverage of ZnO crystals on the substrate in the measuring area, which is further evidenced by the increasing diffraction intensity of the Si 111 peak. The full width at half-maximum (FWHM) values of the main diffraction peak can reflect crystal quality. Narrower diffraction peaks show higher crystallographic quality. The FWHM values of 0 0 0 2 peaks are 0.28^0, 0.25^0 and 0.21^0 for the samples grown from PVP free, 0.1 and 0.5 wt% PVP containing solution, respectively. The narrow FWHM values reveals that the samples are of high crystal quality, and that the quality improved as the weight percent of PVP increases.

On the basis of the morphology and structure analysis, the following mechanism for PVP-assisted electrochemical growth of ZnO prisms is proposed as shown in Fig. 3. In the presence of Zn^{2+} and O_2 in the electrolyte, when the negative potential is applied, hexagonal ZnO crystals are formed at the electrolyte/substrate interface. At the beginning stage of deposition, the growth is three-dimensional [37]. Nonionic PVP molecules would not participate in the electrochemical process but adsorb onto the ZnO facets through chemical interactions with the oxygen (and/or nitrogen) atoms of the pyrrolidone units of PVP. It has been accepted that polymers have different interaction strengths with the atoms on different crystallographic facets [8,29,30], which can lead to the anisotropic growth of a solid material. The high index crystal {1 0 1 0} planes (side facets of hexagonal ZnO columns) have more surface defects than the low index crystal (0 0 0 1) plane (end facets of hexagonal ZnO columns), so we postulate that the side {1 0 $\bar{1}$ 0} planes of ZnO crystals adsorb more PVP than the end (0 0 0 1) plane. Sun et al. [30] recently demonstrated that PVP interacted more strongly with the side face of a silver nanowire than with the ends. In this model, the side facets of ZnO crystals are fully covered by adsorbed PVP through chemical adsorption process and the end side facets are partly covered or uncovered. Therefore, PVP forms a passivated surface of the side facets of ZnO crystals, which inhibits the growth of {1 0 $\bar{1}$ 0} facets and at the same time protects the regularity of the side facets. The uncovered end face of ZnO crystals remain active to the freshly reducing ZnO molecules and subsequent growth on (0 0 0 1) end faces results in the formation of ZnO hexagonal prisms shown in Fig. 3(b).

The addition of PVP not only changed the growth habit of electrodeposited ZnO crystals, but also affected their optical properties. The reflectance spectra of the ZnO films grown from PVP free, 0.1 and 0.5 wt% PVP solutions are shown in Fig. 4. These spectra show similar optical absorbance characteristics in the UV region. The optical band gaps of the three samples calculated from the reflectance spectra have a value of approximately 3.37 eV, which is typical for ZnO material. Differences are observed
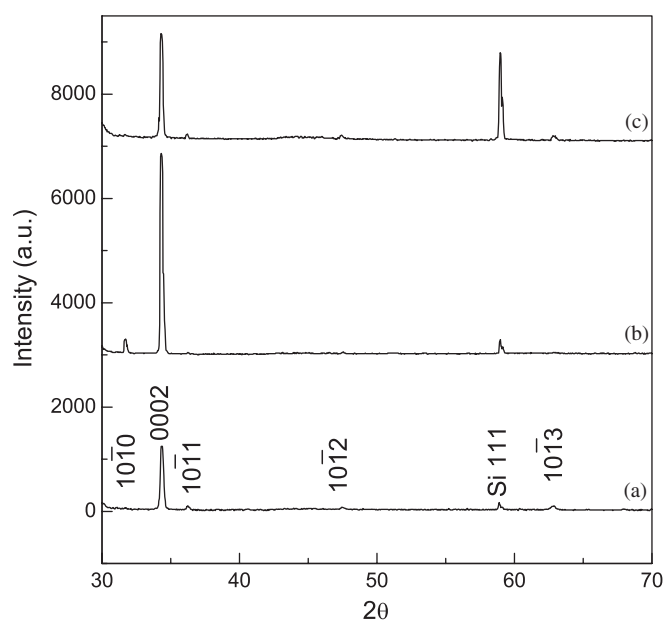
Fig. 2. The XRD pattern of ZnO films grown from deposition bath containing (a) no PVP; (b) 0.1 wt% PVP; and (c) 0.5 wt% PVP.
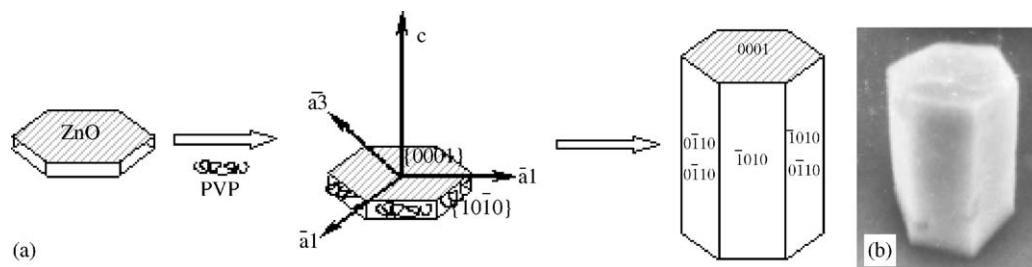
Fig. 3. The Schematic illustration of the possible growth mechanism of ZnO prisms grown from PVP-assisted electrodeposition. (a) The evolution of ZnO hexagonal prisms with the assistant of PVP. The preferential adsorption of PVP onto the side faces of ZnO crystals lead to the anisotropic growth; (b) High magnification SEM image of a single ZnO prism.
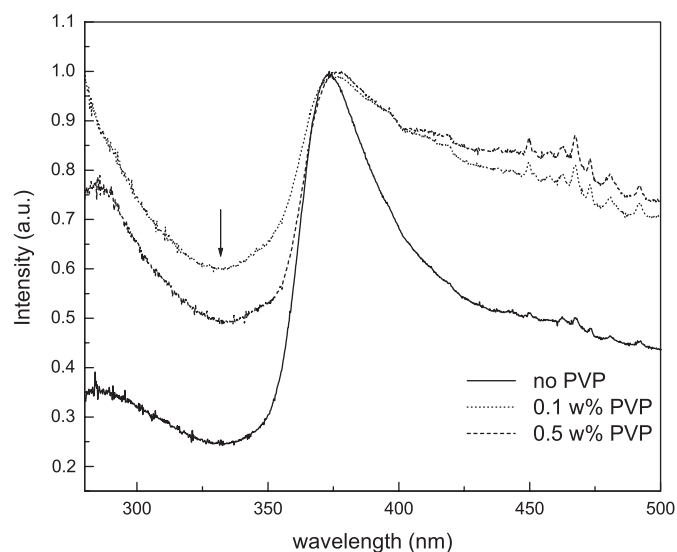

Fig. 4. The reflective spectra of ZnO films grown from deposition bath containing no PVP (solid spectrum), 0.1 wt% PVP (dotted spectrum), and 0.5 wt% PVP (dashed spectrum). The arrow in the figure shows the position of reflectance peak.
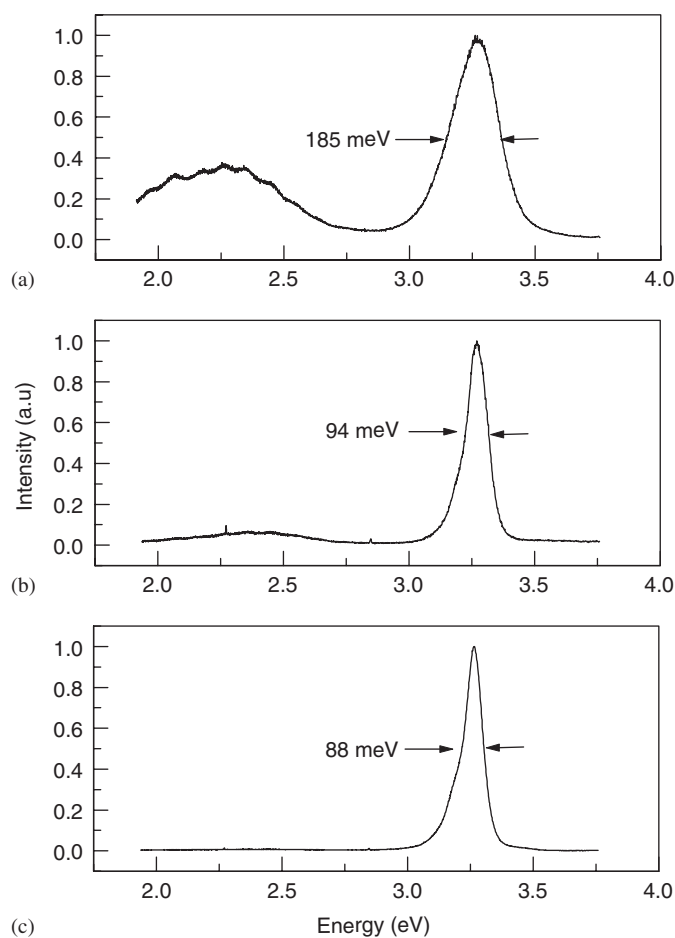

Fig. 5. The room temperature photoluminescence spectra of ZnO films grown from deposition bath containing (a) no PVP; (b) 0.1 wt% PVP; and (c) 0.5 wt% PVP.

in the visible region. For the sample grown from PVP free solution, there is an obvious absorbance in the range 420–500 nm caused by the defects levels. However, for the samples grown in the presence of PVP the defect-related absorbance is very weak, indicating that the ZnO crystals grown with PVP in the bath solutions have lower defects compared with the ones grown without PVP.

Fig. 5 shows the normalized room temperature PL spectra of the samples grown from PVP free, 0.1 and 0.5 wt% PVP solutions. All the spectra consist a narrow UV peak near 3.27 eV and a broader emission band in the green region. The sharp and strong UV emission is ascribed to the free exciton emission, which is consistent with the calculated band gap of the ZnO films. Due to the large size of the ZnO prisms, no obvious shift of the UV emission caused by quantum confinement effects is observed. The linewidth of the UV emission peak decreases obviously, from 185 meV for the PVP free sample to 94 and 88 meV for the PVP assistant samples, which can be comparable to and even better than that of ZnO epilayers [5], indicating good optical quality of these ZnO prisms. Relative to the

PVP free sample, it is observed that the visible emission decreases obviously with addition of 0.1 wt% PVP to the deposition bath. Furthermore, for the sample grown from 0.5 wt% PVP solution the intensity of visible emission (Fig. 5c) was negligible. The visible emission is due to a transition of a photogenerated electron from a shallow level close to the conduction band edge to a deeply trapped hole (a V_o^{**} center) [40]. Surface-trapped hole tunnels back into the particle and recombines with an electron in an oxygen vacancy (V_o^*) resulting in the formation of a V_o^{**}

center. The progressive decrease of deep-level emission indicates that the crystal qualities of ZnO are enhanced. This can be explained by passivation of the ZnO surface by adsorbed PVP, which may reduce the oxygen vacancy sites.

4. Conclusion

To summarize, ZnO hexagonal prisms vertical to Si substrates were fabricated using a simple electrochemical route with addition of PVP into the electrolyte solution. This technology provides a low cost method to grow ordered, aligned hexagonal prisms onto Si substrates without using any external mechanical forces. PVP added into the electrolyte can selectively promote the growth in the vertical direction of the ZnO crystals. The different reactivity of side $\{1\,0\,\bar{1}\,0\}$ facets and end $(0\,0\,0\,1)$ facets of ZnO crystals is attributed to the different absorbance strengths of PVP molecules, leading to the anisotropic growth of ZnO prisms. The reflectance and PL spectra show that ZnO hexagonal prisms grown in the presence of PVP possess excellent optical properties.

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