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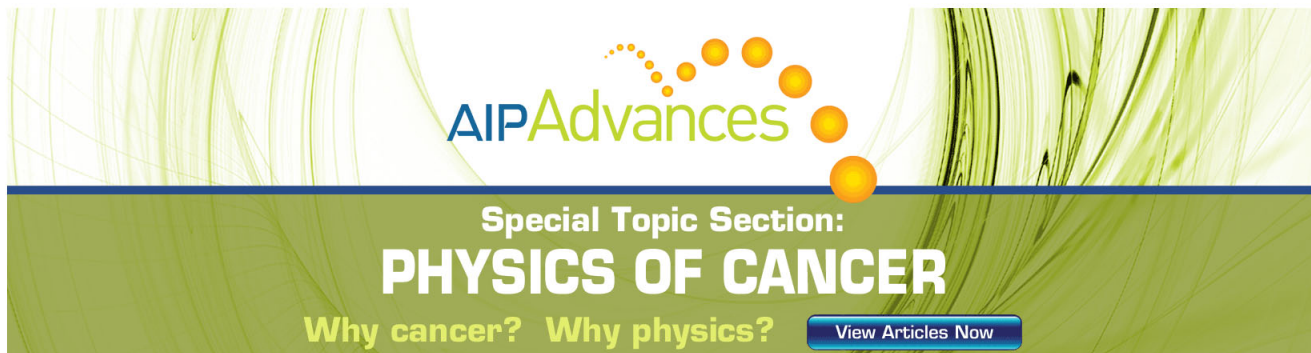
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# The optical properties of ZnO hexagonal prisms grown from poly (vinylpyrrolidone)-assisted electrochemical assembly onto Si (111) substrate

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ZnO hexagonal prisms have been grown from poly (vinylpyrrolidone)-assisted electrochemical assembly onto *p*-type Si (111) substrate. These ZnO prisms arrays are highly (0002) orientated. The (0001) end facets and  $\{10\bar{1}0\}$  side facets of the hexagonal prisms are well defined. The photoluminescence (PL) spectrum of these ZnO prisms shows an intense ultraviolet near band-gap emission with a full width at half maximum of 86 meV at room temperature. The low-temperature PL spectrum is split into well-resolved free and bound exciton emission lines. The temperature dependence of the exciton emission intensities shows a nonmonotonic decaying behavior, which can be explained by the existence of interfacial states. © 2005 American Institute of Physics.

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## I. INTRODUCTION

ZnO has attracted considerable research attention recently because it is a suitable candidate for blue or ultraviolet light-emitting devices and photodetectors. ZnO is a direct wide-band-gap (3.37 eV) semiconductor with a high exciton binding energy of 60 meV. The morphology, size, and orientation of ZnO are crucial to the application of this material. The ZnO random laser created by Cao *et al.* used a highly disordered structure to obtain laser action.<sup>1</sup> Low-dimensional ZnO nanowires can reduce the threshold of stimulated emission because of quantum confinement effects.<sup>2</sup>

In general, fabrication of well-aligned ZnO arrays is an effective route to realize optoelectronic applications. Although aligned growth of inorganic thin films has been successfully achieved by gas-phase techniques such as vapor transport<sup>2,3</sup> and chemical-vapor deposition,<sup>4,5</sup> these techniques inevitably need high vacuum or high temperature, making them disadvantageous for large-scale production. On the other hand, wet chemistry route is a cheap and flexible method to synthesize ZnO nanomaterial with a specific shape, but it may suffer from contamination issues, which limits the application.

We develop a low-temperature and template-free polymer-assisted electrochemical route to grow highly (0002)-oriented arrays of ZnO hexagonal prisms onto *p*-type Si (111) substrates. Poly (vinylpyrrolidone) (PVP) was added into the deposition bath to modulate the growth of ZnO crystals. It has been reported that ZnO nanorods with hexagonal faces can be directly electrodeposited from O<sub>2</sub>-saturated zinc chloride aqueous solution.<sup>6,7</sup> While these nanorods were short in length, and overlapped, which were difficult to be used in practical applications. The use of PVP in the deposition bath can effectively promote the vertical growth of ZnO crystals and disperse the nucleation of ZnO nanorods. The detail of PVP-assisted formation of ZnO hexagonal prisms has been reported elsewhere,<sup>8</sup> and it is strengthened on the optical properties of these prisms in this paper. The optical investigation shows that the ZnO prisms are of high crystal quality and have attractive optical properties. Using Si as the substrate provides the possibility to integrate these high-quality hexagonal prisms with silicon-based devices.

## II. EXPERIMENT

The deposition solution was O<sub>2</sub>-saturated aqueous solutions, consisting of 0.005-M ZnCl<sub>2</sub>, 0.1-M KCl, and 0.5 wt % PVP. The experiment was carried out potentiostatically at -0.6 V (versus Ag/AgCl reference electrode) for

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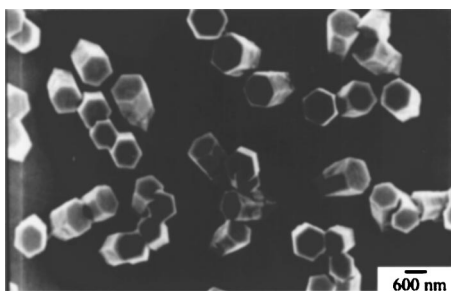


FIG. 1. SEM photos of ZnO grown from PVP-assisted electrodeposition.

1 h. Solutions were held at 60 °C during deposition. The substrate was *p*-type, (111)-oriented Si wafer. Before electrodeposition the substrate was sequentially ultrasonically cleaned in acetone, ethanol, and water, respectively, each for 10 min. Then the Si wafer was immersed in a 5% HF solution for oxide removal followed by rinsing with doubly distilled water. After deposition, the film was rinsed thoroughly with ethanol and distilled water, which was essential to remove PVP absorbed onto ZnO surfaces.

The morphology of the film was investigated by a Hitachi S 4200 field-emission scanning electron microscopy. The x-ray diffraction (XRD) spectra were measured using a rotating anode x-ray diffractometer with Cu  $K_{\alpha 1}$  radiation of 1.541 Å. The photoluminescence (PL) measurements were carried out in the temperature range from 83 to 283 K using the 325-nm line of a He–Cd laser as the excitation source. The surface photovoltage spectroscopy (SPS) was measured by applying a monochromatic light (obtained by passing a light from a 500-W xenon lamp through a double-prism monochromator) on a sample. A lock-in amplifier, synchronized with a light chopper, was employed to amplify the photovoltage signal.

### III. RESULTS AND DISCUSSION

PVP added into the deposition bath plays an important role in modulating the growth of electrodeposited ZnO. Figure 1 shows the scanning electron microscopy (SEM) image of ZnO crystals grown from deposition solutions containing 0.5 wt % PVP. Uniform ZnO hexagonal prisms are observed to grow along  $\langle 0001 \rangle$  orientation. The (0001) end facets and the  $\{10\bar{1}0\}$  side facets are clearly identifiable. The growth mechanism of ZnO hexagonal prisms from PVP-assisted electrochemical assembly can be briefly explained as follows: PVP molecules adsorb preferentially onto the  $\{10\bar{1}0\}$  side facets, leaving the (0001) end facets active to the fresh ZnO molecules and promoting the growth in the  $\langle 0001 \rangle$  direction.<sup>8</sup> Such separated and aligned hexagonal structure on Si substrate provide potential application in many fields. The well-faceted nature of these prisms with two naturally faceted hexagonal ends can provide a natural resonance cavity for stimulated emission.<sup>2</sup> If these prisms are micropatterned to fabricate specific geometry, they can be used in functional devices.

The XRD spectrum of ZnO crystals grown from PVP-assistant sample is dominated in the (0002) orientation,

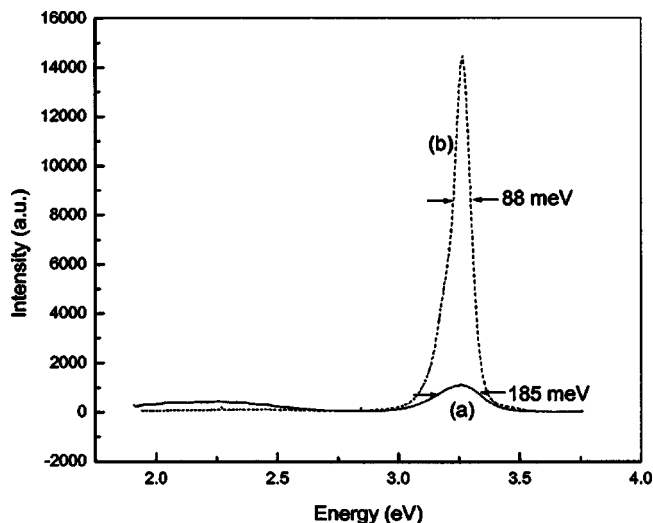


FIG. 2. Room-temperature PL spectra of ZnO grown without (curve a, straight line) and with PVP (curve b, dash line).

which is consistent with the SEM results. The full width at half maximum (FWHM) is 0.21°, implying super crystal quality.

Because these hexagonal ZnO prisms have potential application in the photoelectric devices, more attention is paid to the optical properties. Figure 2 shows the room-temperature PL spectra of the samples grown without and with PVP. Compared with the non-PVP sample, some obvious differences can be observed. The intensity of the near band-gap exciton emission at 3.27 eV of the PVP-assistant sample increased significantly. The FWHM value of this peak evidently narrows from 185 to 88 meV. This value can be comparable with those of ZnO thin films grown by the method of molecular-beam epitaxy, and even narrower.<sup>9,10</sup> The increasing peak intensity and decreasing peak linewidth imply that the quality of the PVP-assistant sample is significantly enhanced. Another change is that the intensity of the visible emission decreases obviously for the PVP-assistant sample. The origin of the visible emission is generally accepted as the transition of a photogenerated electron from a

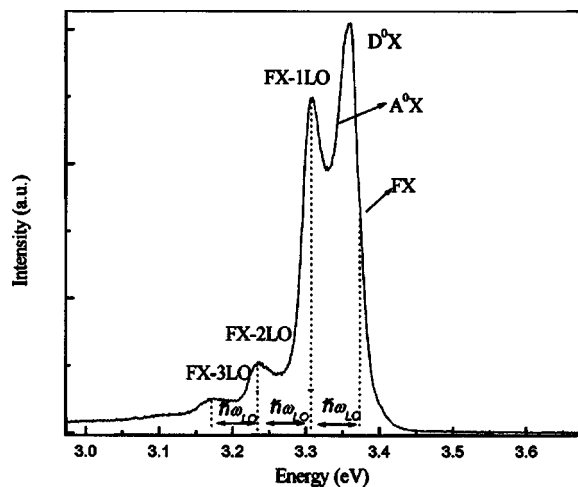


FIG. 3. Low-temperature PL spectrum of the PVP-assistant ZnO hexagonal prisms at 83 K.

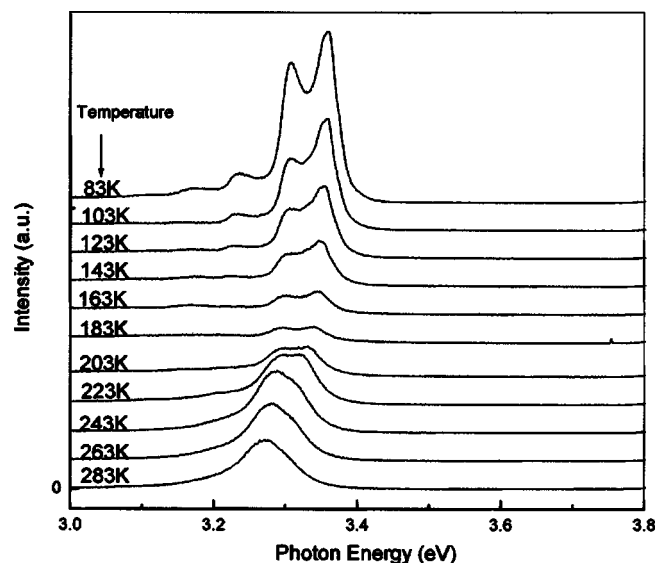


FIG. 4. Temperature-dependent PL spectra of PVP-assistant ZnO hexagonal prisms.

shallow level close to the conduction-band edge to a deeply trapped hole (a  $V_o^{**}$  center).<sup>11,12</sup> Surface-trapped hole can tunnel back into the particle, where it recombines with an electron in an oxygen vacancy ( $V_o^*$ ) resulting in the formation of a  $V_o^{**}$  center, the recombination center of visible emission. In terms of experimental results, two reasons are contributed to the decrease of the visible emission. One is that the crystal quality of PVP-assistant sample is enhanced which reduces the number of defects inside the crystals. The other reason is that, PVP molecules adsorb onto the side facets of ZnO crystals during electrodeposition, which decreases the number of oxygen vacancy sites adsorbed on ZnO facets. These two effects would prevent the formation of  $V_o^{**}$  to decrease the recombination centers of visible emission, as a result, decreasing the intensity of the visible emission.

Figure 3 shows the low-temperature (83 K) UV PL spectrum of the PVP-assistant ZnO prisms on Si substrate. The UV emission is split into a series of lines, which was not observed in the sample grown without PVP. The strongest peak at 3.360 eV is characteristic of neutral-donor bound exciton ( $D^0X$ ). The emission observed at 3.374 eV on the higher-energy shoulder of the  $D^0X$  peak is assigned to the free exciton (FX). The weak emission shoulder at the

lower-energy side of  $D^0X$  located at 3.345 eV indicates the contribution of neutral-acceptor bound exciton ( $A^0X$ ). The peaks at 3.307, 3.236, and 3.167 eV are attributed to the 1-LO, 2-LO, and 3-LO phonon replica of FX, respectively. Well-resolved excitonic lines further demonstrate that this sample is of high quality since imperfect crystals would broaden the emission band and lower the emission intensity.<sup>9,13</sup>

Figure 4 shows the temperature-dependent PL spectra of the ZnO hexagonal prisms measured from 83 to 283 K. The exciton emission of FX,  $D^0X$ , and  $A^0X$  show an obvious redshift with increasing measurement temperature. The temperature dependence of the maximum peak energy of FX,  $D^0X$ , and  $A^0X$  is shown in Fig. 5(a). The temperature dependence of the exciton emission energy is related to the temperature dependence of the band energy, which can be expressed in terms of the semiempirical formula:  $E_x(T) = E_x(0) - \alpha T^2 / (T + \beta)$ ,<sup>14</sup> where  $E_x(0)$  is the peak energy at absolute zero temperature and  $\alpha$  and  $\beta$  are the fitting parameters.  $E_x(0)$  is 3.378, 3.365, and 3.345 eV, respectively, for FX,  $D^0X$ , and  $A^0X$  emissions. In Fig. 5(a), the lines represent the calculated temperature dependences for each emission mode and it can be shown that the calculated lines can fit well with the experimental data.

The temperature dependence of  $D^0X$  and FX emission intensities is plotted in Fig. 5(b). As can be seen from Fig. 5(b), it is different from the exponentially decaying behavior reported previously.<sup>9</sup> The intensities firstly decrease with increasing the temperature in the range of 83–183 K, then increase with temperature in the range of 183–233 K, and decrease again at temperature  $T > 233$  K. The nonmonotonic temperature behavior of the PL intensity may be caused by the interface states, formed by the intersecting of the hexagonal prisms, as shown in Fig. 1. The formation of interface states can be proven by the measurement of SPS. SPS is a well-established nondestructive technique for semiconductor characterization that relies on analyzing illumination-induced changes in the surface voltage. It is an effective tool to investigate the photophysics of excited states generated by absorption in the aggregate state.<sup>15</sup> Figure 6 gives the SPS of the PVP-assistant ZnO sample. The sample shows an intense surface responses peak at 392 nm, which implies the existence of interface states. When the light was applied on the sample, photogenerated electrons and holes will accumulate

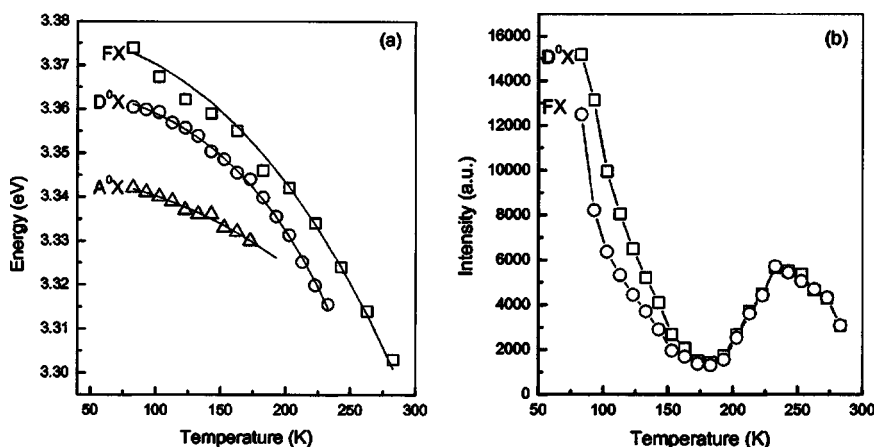


FIG. 5. Temperature dependence of (a) excitonic emission energies and (b) excitonic emission intensities of the ZnO hexagonal prisms. ( $\square$ ) represents FX emission, ( $\circ$ )  $D^0X$ , and ( $\triangle$ )  $A^0X$ .

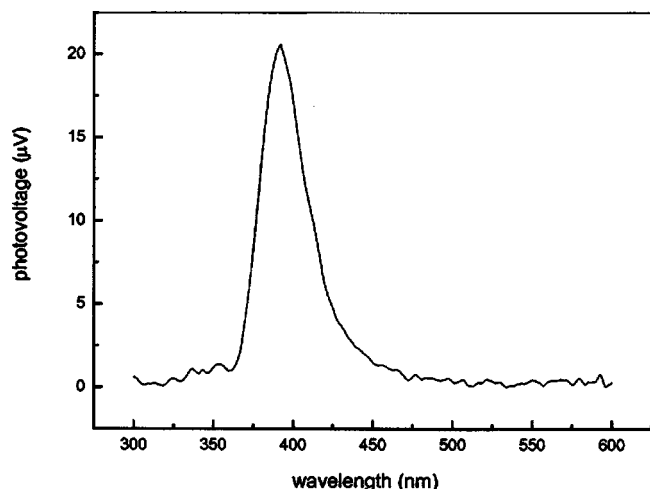


FIG. 6. Surface photovoltage spectroscopy of PVP-assisted ZnO hexagonal prisms.

at the band bend due to the existence of the interfacial states, as a result, the surface photovoltage signal can be observed. The SPS peak at 392 nm is near the band gap of ZnO crystals.

As temperature is below 183 K, the intensity of the excitonic emissions decreases with increasing temperature, caused by the increasing thermal release of excitons, similar to other reports.<sup>9</sup> The electrons trapped at the interface states will not contribute to the radiative recombination. With increasing temperature at  $T > 183$  K, trapped electrons are partly relaxed from the interface states, resulting in an increase of free electrons. This means that the number of excitons will increase at the same time. In this temperature range, the two processes of thermal release of excitons and the increase of excitons exist simultaneously, while the latter is dominant. Therefore, the increasing intensity of excitonic emission is observed. When the temperature is over 233 K, most electrons trapped at the interface states are thermally ionized, the excitonic emission thermally quenched becomes dominant. The intensity of exciton emission decays again with increasing temperature.

#### IV. CONCLUSION

In conclusion, a new method of PVP-assisted electrochemical assembly has been developed for growing directional ZnO hexagonal prisms on Si substrate. The ZnO prisms show favorable improvement in the crystal quality, defect density, and luminescence properties. The temperature-dependent behavior of the PL intensity shows an interesting nonmonotonic decaying characteristic, which can be explained by the existence of interface states.

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