Effects of AlO_x-cap layer on the luminescence and photoconductivity of ZnO thin films

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The effects of AlO_x-cap layer on the optical and photoelectrical properties of ZnO films have been studied by cathodoluminescence (CL), photoluminescence (PL), and photoconductivity (PC). Both the PL and CL show that the cap layer improves the emission characteristics of ZnO by enhancing the band-edge emission while at the same time reducing the deep-level emissions. To study the origin of improvement, depth-resolved CL has been carried out to map out the emissions at different depths. It shows that the improvement occurs primarily at the film surface, which indicates the cap layer acts as a passivation layer that suppresses the detrimental surface states. The PC measurement on the capped ZnO at room temperature shows a distinctive excitonic feature at 3.29 eV and an overall increment of photoresponse above the band gap. Therefore, our results suggest a higher sensitivity of UV detection can be achieved in ZnO simply be employing a thin AlO_x-cap layer. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1900945]

ZnO has recently been attracting considerable attention due to its potential applications in short-wavelength optical technology.[1] Its wide band-gap (3.3 eV) and high-excitonic binding energy (60 meV) has made ZnO become one of the promising candidates for making various UV optoelectronic devices such as light emitting diodes,[2] laser diodes,[3] photodetectors,[4] etc. However, to increase the performance of these devices, detrimental surface defect states have to be suppressed or eliminated. For example, concerning the UV detection, surface recombination plays a major role in governing the photoresponse due to the short penetration depth of photons at energies above the band gap. Higher surface recombination velocity reduces the photocurrent generation and therefore lowers the sensitivity.[5] Thus, to develop an appropriate method to effectively passivate the unwanted surface states will greatly increase the functionalities of ZnO.

In this Letter, we report the effects of the AlO_x-cap layer on ZnO thin films. Cathodoluminescence (CL), photoluminescence (PL), and photoconductivity (PC) have been used to study the luminescence and photoresponsivity of ZnO with and without the cap layer. Results show that the cap layer effectively enhances the band-edge emission of ZnO by 3–5 times while at the same time reduces the deep-level (DL) emissions. Depth-resolved CL taken at different accelerating voltages shows that the emission profile improved more at the film surface than in the interior, which suggests the unwanted surface states are being suppressed by the cap layer. Finally, compared with the bare counterpart, a higher photocurrent is observed from capped ZnO at above the band-gap region, which indicates higher UV sensitivity.

The samples are grown on (001) Si or SiO_2/Si substrate by magnetron sputtering of metallic Zn and Al targets at 150 W.[6] A mixture of Ar and O_2 at 6 mTorr and a growth temperature of 550 °C are used for ZnO growth. For AlO_x capping, a metallize shadow mask is used to cover half of the film and AlO_x is then grown on the exposed region so that direct comparison can be made between the two regions. The cap layer is grown in an O_2 ambience at room temperature. The film is then rapid thermal annealed at 300 °C under 5 Torr O_2 for 2 min. X-ray photoelectron spectroscopy (Ulvac–Phi, Quantera) reveals that the O to Al ratio in AlO_x varies from 1.4 to 1.5. CL is conducted in a scanning electron microscope equipped with an Oxford MonoCL spectrometer and an Andor charge-coupled device (CCD) detector.[7] The probe current is calibrated by using Faraday cup before and after the experiments. For depth-resolved experiments, a fixed excitation power of 3 μW is used so that a constant generation of electron-hole pair is ensured at different depths. In addition, a low power is used to avoid the electron-beam-induced effect on the emissions of capped ZnO.[6] For the photoluminescence, a HeCd Kimmon 325-nm laser together with a 0.25 m spectrometer and a CCD detector are used. Photoconductivity is conducted by using a dispersed light, generated by an Oriel 150 W Xe arc lamp, irradiated on the ZnO films coated with a pair of Ohmic Ti/Au parallel electrodes. An optical chopper with 100 Hz and a Standford Research lock-in amplifier are used for data acquisition. Prior to the measurements, the samples are kept in the dark for two days to reach the dark current. A 3-V dc bias is applied to the films during the measurements. The microstructure of the sample is studied by a JEOL 2010 transmission electron microscope (TEM). All the measurements are carried out at room temperature.

The samples are first examined by cross-section TEM. As illustrated in Fig. 1(a), it shows that the ZnO film is highly *c*-axis textured with columnar growth characteristics. On the other hand, the AlO_x-cap layer is in an amorphous structure with the thickness of ~7–10 nm. Both the CL and PL show that the emission characteristics of ZnO are improved after capping with AlO_x. Figure 1(b) shows the CL spectra of bare and capped regions collected from the same ZnO film taken at 4 kV and 750 pA. Direct comparison between the two spectra indicates a fourfold increase in the

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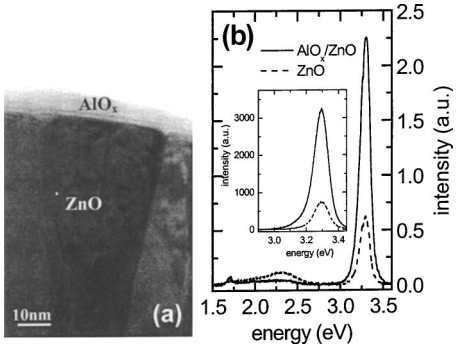

FIG. 1. (a) The cross-section TEM image of AlO_x/ZnO. (b) The CL spectra of AlO_x-capped (solid) and bare (dash) ZnO film. The PL spectra are shown in the inset.

band-edge emission at 3.29 eV after capping. In addition, the DL emission band at 2.3 eV reduces slightly. Similar conclusions can be drawn from the PL data as shown in the inset. In order to find out the root cause of the enhancement, we have performed the depth-resolved CL on two regions. Since the film thickness is on the order of 300 nm, the Kanya–Okayama model deduces an electron beam of 6 kV will reach the film–substrate interface.[8] Therefore excitations below 6 kV should arise mostly from the film bulk while those above 6 kV will come from both the film and substrate. Figures 2(a) and 2(b) show the CL spectra of the bare and capped regions taken at various accelerating voltages from 2 to 11 kV. We have determined the intensities of the band-edge and DL emissions at each voltage by using a Gaussian fitting routine and their variations with depth are illustrated in Figs. 2(c) and 2(d). From 2 to 3.5 kV, which corresponds to the depth of 50–100 nm, the surface effect is more prominent and we see that the band-edge emission of the two regions increases with depth, indicating the surface states are present and that their influence lessens with increasing depth.[9] However, comparing the emission intensity between the bare and the capped regions, it is obvious that the emission that arises from the capped region is higher due to the reduction of surface states. Above 4 kV, a steady decrease of intensity in both regions occurs, which can be attributed to

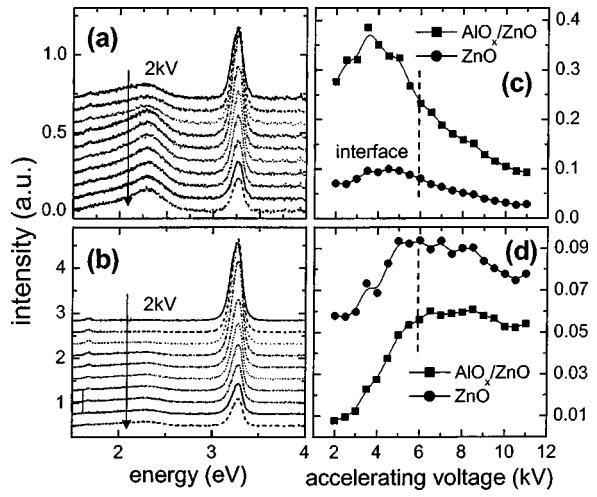

FIG. 2. Depth-resolved CL spectra of (a) bare and (b) capped ZnO film. The arrows indicate the accelerating voltages increased from 2 to 11 kV. The variation of (c) band-edge and (d) DL emission intensities with accelerating voltage. The square symbol represents AlO_x/ZnO while the circle represents bare ZnO.

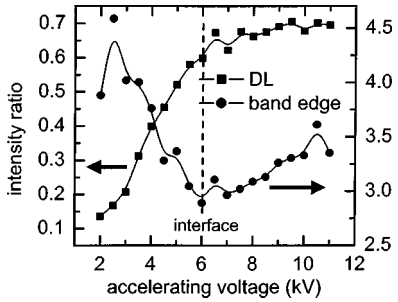

FIG. 3. The band-edge (circle) and DL (square) intensity ratios of capped/bare ZnO.

the reabsorption of light into the films. Internal absorption has been reported to affect the band-edge CL of semiconductors.[10] It reduces the emission intensity at higher beam voltages due to the presence of the Urbach tail.[10] Nonetheless, the overall intensity of the capped region remains higher than that of the bare counterpart. On the other hand, due to the small absorption coefficient of ZnO below the band gap, internal absorption is not significant in DL emissions.[9] Therefore, depth-resolved CL should exhibit the actual DL emissions under constant power. Figure 2(d) shows that the general DL intensity profile of the capped ZnO is lower than that of the bare ZnO, in particular at the surface region where the intensity is greatly reduced to only ~0.01, indicating the DL recombination centers are being passivated. Assuming the AlO_x layer is transparent at photon energies of 1.5–3.5 eV, which is confirmed by the UV-vis-IR transmission, we have determined the intensity ratios of the band edge and DL of capped/bare to account for the capping effect. The results are shown in Fig. 3. It is seen, indeed, that the ratio of the band edge is higher at the surface than that in the film interior, whereas the ratio of the DL is lower, which agrees well with our interpretation.

The cap layer also improves the photoresponse of ZnO films. Figure 4 illustrates the photocurrent spectra of the bare and capped regions. The bare spectrum is found to be consistent with the literature.[11] The current ratio of capped/bare is shown in the inset. From the photocurrent spectra, the photocurrent generated below the band gap is very low and it arises mostly from the film bulk. However, as the photon energy increases, the penetration depth decreases and high-energy photons thus become more surface sensitive. Any detrimental recombinations that occur at the surface will reduce the magnitude of photocurrent. We see that when the photon energies are above the band gap, an increase of photocurrent ratio is clearly observed. In fact, that the ratios are greater than 1 above gap indicate the surface recombination velocity

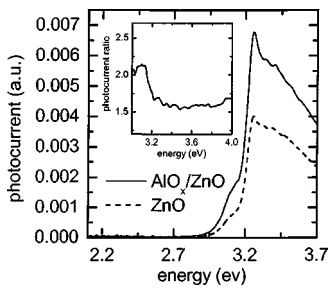

FIG. 4. The photocurrent spectra of capped (solid) and bare (dash) ZnO. The inset shows the photocurrent ratio.

is lowered. Finally, since an excitonic peak can be clearly seen from the spectra, it indicates the band-edge emission obtained from PL and CL are most likely due to the excitonic transition.

Using an oxide layer to improve the surface conditions has been reported in other semiconductors such as GaAs and Si.[12] In ZnO, it is expected the surface usually contains undercoordinated Zn cations that accommodate a high density of oxygen vacancies.[13] As oxygen vacancies are known to produce DL emissions,[14] an oxide cap layer in this case may passivate the oxygen deficiency sites and thus increases the band-edge emission as well as improves the above-gap photoresponse.

In summary, the effects of AlO_x on the optical and photoelectrical properties of ZnO films have been studied by CL, PL, and PC. Both PL and CL show that the cap layer improves the emission from ZnO by passivating the surface states. PC shows a dramatic increase of photoresponse in capped ZnO above the band gap indicating surface recombination indeed is lowered. Our results illustrate that a thin layer of AlO_x can effectively increase the sensitivity of ZnO for UV detection.

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