Temperature dependence of surface and structure properties of ZnCdO film*

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$Zn_{1-x}Cd_xO$ films are grown on *c*-sapphire substrates by laser molecular beam epitaxy (LMBE) at different temperatures. Their crystallographic structures, compositions, surface electronic structures are investigated. The *a*-axis lattice constant of $Zn_{0.95}Cd_{0.05}O$ is 3.20 Å. Moreover, the epitaxial relationship shows a 30°-in-plane rotation of the film with respect to the c-sapphire substrate. When the substrate temperatures arrives at 500 °C, the *in situ* reflection high-energy electron diffraction (RHEED) pattern of ZnCdO film shows sharp streaky pattern. The maximum Cd content of ZnCdO film grown at low substrate temperatures increases up to about 29.6 at.%, which is close to that of the ceramic target. *In situ* ultraviolet photoelectron spectroscopy (UPS) measurements demonstrate that ZnCdO film exhibits intense peaks at 4.7 eV and 10.7 eV below the Fermi level, which are assigned to the O 2p and Zn 3p states. Energetic distance between Zn 3d and Cd 4d is 0.60 eV. Above 470 nm, the thin film shows excellent optical transmission.

Keywords: surface structure, ZnCdO films, laser molecular beam epitaxy

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1. Introduction

The epitaxial growth of ZnO related materials is a worldwide rapidly developing research field driven by their potential for various optoelectronic applications, owing to their direct wide band gap (3.37 eV) and the large exciton binding energy (60 meV).[1–4] Recently, an important step in order to design ZnO-based devices is to realize the band gap engineering for creating the quantum wells in device heterostructures. This wavelength tunability was accomplished by growing $Zn_{1-x}Mg_xO$[5–8] and $Zn_{1-x}Cd_xO$[9–13] alloys, which show wider or narrower band gap energies than ZnO, respectively. By alloying with CdO, which has a cubic structure and narrower direct band gap of 2.3 eV, the band gap of ZnO could be ultraviolet shifted to visible light spectra range. The narrowing of the band gap is also desirable to tune the emission wavelength of future optoelectronic devices into the visible range. The previous researches showed that the films with different amounts of Cd content were fabricated at various substrate temperatures.[14] The single-phase $Zn_{1-x}Cd_xO$ layers with 7%Cd were grown by pulsed-laser deposition (PLD), resulting in the narrowing of the band gap of 0.3 eV.[15] Later work has claimed an incorporation of Cd of 8.7% without indication of phase separation. The band gap of ZnCdO alloy has been reported to decrease accompanied by an increase in Cd concentration. The structural disorder and the potential energy fluctuation have also been shown as the concentration of the alloyed atoms is increased. However, the surface morphology, especially the electronic structure of Cd in $Zn_{1-x}Cd_xO$ film is not very detailed by laser molecular beam epitaxy (LMBE). In what follows, we explore the most appropriate temperature for the LMBE fabrication of single-phase ZnCdO epilayers. We have obtained the detailed results of the surface and electronic states of ZnCdO films by *in situ* X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS). The X-ray diffraction (XRD) and atomic force microscopy (AFM) show a *c*-axis rotation and good surface. This relationship corresponds to a 30°-in-plane rotation of the film with respect to the substrate. It is found that the most appropriate temperature for ZnCdO deposition is 500 °C. The Cd concentration in the ZnCdO alloy can be systematically adjusted by changing the substrate temperature. The transmission spectra of the thin films exhibit an abrupt decrease below about 400 nm.

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2. Experimental details

Epilayers ZnCdO films were prepared on *c*-plane sapphire substrates by LMBE with an energy density 2 J/cm^2–3 J/cm^2. A ceramic target of $Zn_{0.7}Cd_{0.3}O$ was used. A KrF excimer laser (248 nm, 20 Hz, and 25 ns) was used as an ablating source. The background pressure was 1×10^{-7} Pa and the substrate was mounted 5 cm away from the target in the ultrahigh vacuum (UHV) deposition chamber. The substrate was annealed at 650 °C for 90 min to obtain a prefect interface. Then, the substrate temperature was lowered to various substrate temperatures and kept constant in the film growth process. The ZnCdO films were grown in 0.5-Pa pure oxygen and in a substrate temperature range of 200 °C–600 °C. After deposition, the 30-min annealing treatment *in situ* was carried out to improve the interface. The crystalline surface structure of the $Zn_{1-x}Cd_xO$ film was monitored using RHEED at an electron acceleration voltage of 25 kV and an incidence angle of 1°–3° with respect to the sample surface. The duration of the $Zn_{1-x}Cd_xO$ film growth was one hour and the laser frequency was kept at 2 Hz, resulting in a film thickness of 200 nm. Then, the samples were transferred into an ultra high vacuum analysis chamber equipped with an X-ray and UV-source. XPS and UPS measurements were performed using an Al Kα X-ray source at 1486.6 eV and He discharge lamp at 21.2 eV (He I), respectively. For all measurements presented here, the Al Kα line with a photon energy of 1486.6 eV was used. XPS/UPS measurements were conducted under an ultrahigh vacuum of 3×10^{-8} Pa. Each spectrum of emitted electrons was recorded at a resolution of 0.1 eV.

3. Results and discussion

Figure 1 shows *in situ* RHEED patterns at various substrate temperatures, corresponding to the parameters under which many epitaxial oxides are typically grown. The growth is carried out in a wide range of substrate temperature from 200 °C to 600 °C. A sharp streaky pattern of the Al_2O_3 (0001) substrate is observed after thermal annealing. Several Bragg-reflection spots are superposed on sharp streak diffraction at lower temperatures, suggesting that the films grow in the Stranski–Krastanov growth mode.[9] When the substrate temperature rises up to 500 °C, the RHEED pattern of ZnCdO film shows sharp streaky pattern (Fig. 1(c)). At higher temperature, the RHEED pattern of ZnCdO shows Bragg-reflection spots again. When the substrate temperature exceeds 600 °C, RHEED of ZnCdO surface (Fig. 1(d)) exhibits broad diffraction rings. The curves 1 and 2 in Fig. 1(e) represent the diffraction intensities along the vertical spacing. The RHEED patterns are measured along the $[1\bar{1}00]$ azimuths of Al_2O_3 substrate and ZnCdO film respectively. The in-plane lattice parameter is deduced by the distance between the $[\bar{1}0]$ and [10] streaks on the fluorescent screen. If we define the distance between the (−1 0) and (1 0) Al_2O_3 diffraction orders as "*b*" shown in curve 2, the vertical distance for the ZnCdO diffraction spots is equal to 1.16*b*. It corresponds to the lattice constant of $a = 3.20$ Å in real space. This relationship corresponds to a 30°-in-plane rotation of the film with respect to the substrate (Fig. 1(f)). This 30°-rotation strongly suggests that the epitaxial relationship is dictated by Al–O bonding at the interface. The epitaxial relationship is the same as that for group III-nitrides grown on [0001] sapphire substrate.[10] The mismatch of rotational symmetry at the interface can be explained by Marius Grundmann's theory.[16] The theory is as follows:

$$N_{\mathrm{RD}} = lcm(n,m)/m \quad n,m \in \{1,2,3,4,5,6\}, \tag{1}$$

$$\phi_k = 2\pi k/lcm(n,m)/m, \quad \text{where } k \text{ is an integer.} \tag{2}$$

The substrate surface and epilayer have C_n and C_m symmetry, respectively, with respect to the surface normal. $lcm(n,m)/m$ is the least common multiple of n and m. Φ_k is rotation angles. In this case, $m = 6$ and $n = 6$, so the N_{RD} is 1 and there is 30°-rotation angle between Al_2O_3 (0001) and ZnCdO (0001). The RHEED pattern is measured for ZnCdO along the $[11\bar{1}0]$ azimuth shown in Fig. 1(g). The sharp streaky patterns $[1\bar{1}00]$ and $[11\bar{2}0]$ of ZnCdO demonstrate that 500 °C is the most suitable temperature for ZnCdO deposition by LMBE.

Figure 2 shows the different amounts of Cd content of ZnCdO layers. It is obvious that the Cd content decreases with the increase of substrate temperature. Experimentally, we can make the Cd percentage of the $Zn_{1-x}Cd_xO$ film tunable by adjusting the substrate temperature. Due to substantially reduced desorption rate of Cd, it is much helpful for the Cd-rich growth at lower temperature. In this experiment, the maximum Cd content of ZnCdO film grown at 200 °C increases up to about 29.7 at.%, which is close to the target content and Lange *et al.*'s result.[17] However, it is significantly larger than that of Yang *et al.*'s result.[14] When the substrate temperature increases to 300 °C, the Cd content in the alloyed films was much lower than that in the target, due to the difference in vapor pressures between Cd and Zn. In Fig. 2, the content of Cd in the alloyed film is very consistent with the Yang *et al.*'s result[14] with the substrate temperature rising up to 300 °C. The Cd content deduced from EDS is about 0.8% higher than that from XPS above 300 °C. At the lower temperature the Cd content from XPS is very consistent with that from EDS. The difference is due to the slow cooling process, which could make the Cd content desorbed at higher temperature. It is predictable that the Cd content in ZnCdO film will increase further when optimized growth conditions are realized by tuning the substrate temperature, the target content, the chamber pressure, etc.

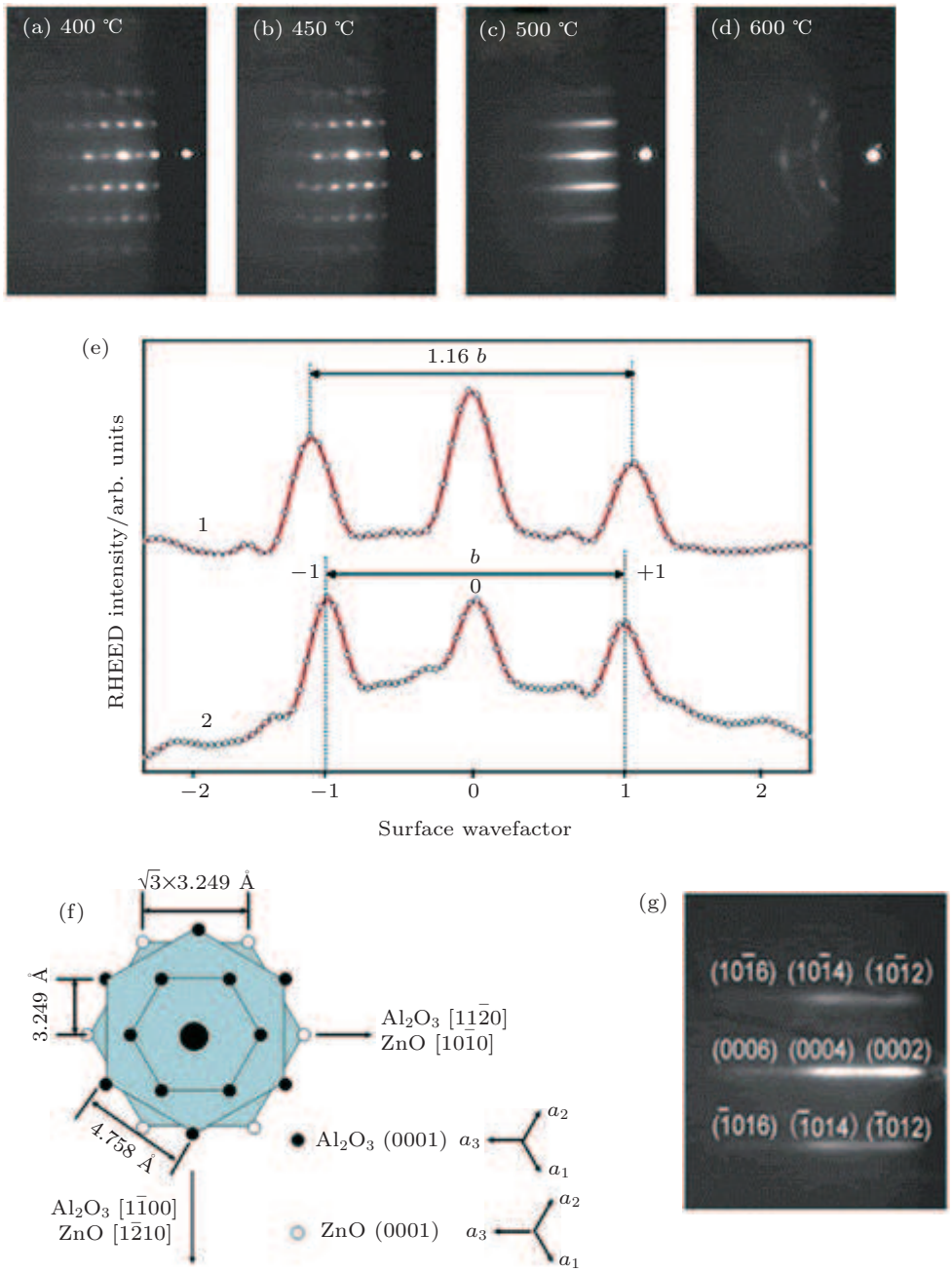


Fig. 1. (color online) (a)–(d) RHEED patterns of ZnCdO [1$\bar{1}$00], (e) horizontal line scans (curve 1) for Al_2O_3 [1$\bar{1}$00] and (curve 2) for $Zn_{0.95}Cd_{0.05}O$ respectively, (f) epitaxial relationship of $Zn_{1-x}Cd_xO$ on Al_2O_3 (0001), and (g) RHEED pattern measured for ZnCdO [11$\bar{2}$0] at 500 °C.

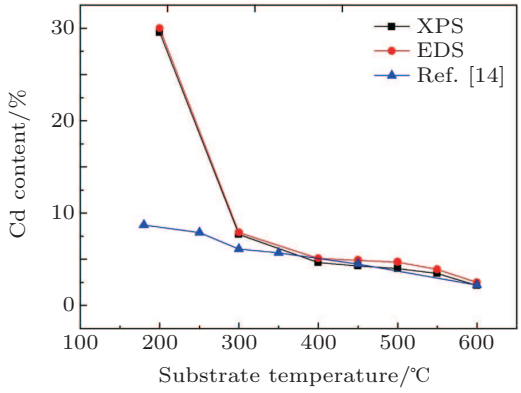


Fig. 2. (color online) Variations of Cd content with substrate temperature, deduced from *in situ* XPS and EDS.

The Zn $2p_{3/2}$ and $2p_{1/2}$ core levels are also detected at 1022.3 eV and 1044.3 eV, respectively. Figure 3 shows the Cd 3d range of an *in situ* XPS analysis of the ZnCdO films. All evaluated full width at half maximum (FWHM) values are shown in the inset of Fig. 3. It follows from the inset that an average FWHM is about 1.0 eV at different temperatures. The signal of the Cd $3d_{5/2}$ peak contribution is observed at 405.4 eV, which can be attributed to Cd^{2+}state.[12] The energetic distance between Cd $3d_{3/2}$ and Cd $3d_{5/2}$ amounts to 6.7 eV. Figure 4(a) shows *In situ* UPS measurements of the ZnCdO films, each of which exhibits intense peaks at 4.7 eV and 10.7eV below the Fermi level. The peaks in a binding

energy range of 3 eV∼7 eV are the valence bands of ZnCdO, including O 2p states mainly.[18,19] Additionally, a new signal develops at 10.7 eV below the Fermi level, corresponding to the photo-emission of Zn 3d valence band. The Zn 3d position is found to shift gradually towards the lower energy at 500 °C and 550 °C. Zn 3d signal is also found in the XPS survey spectrum. Variable photon energy band spectra of ZnO in a range of 31 eV–1253.6 eV were fitted with four Gaussian peaks,[20] among which one peak relates to the Zn3d states, and the other three peaks are contributed by O2p band spectra. Figure 4(b) shows the detailed spectrum of the ZnCdO film in a binding energy range of 9.1 eV–12.6 eV at 525 °C. It comes from two contributions. The signal at 10.52 eV (denoted by Zn 3d) is assigned to Zn forming the ZnCdO film. The second peak at the high binding energy shoulder is denoted by Cd 4d. Its relative energetic distance between Zn 3d and Cd 4d is 0.60 eV.

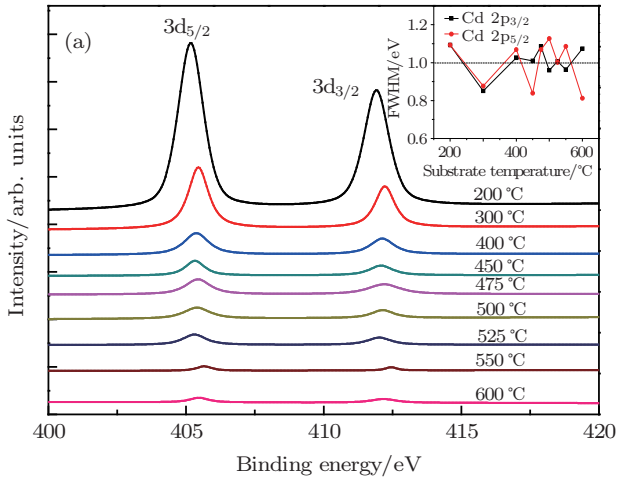


Fig. 3. (color online) *In situ* XPS detailed spectra of Cd 3d of ZnCdO.

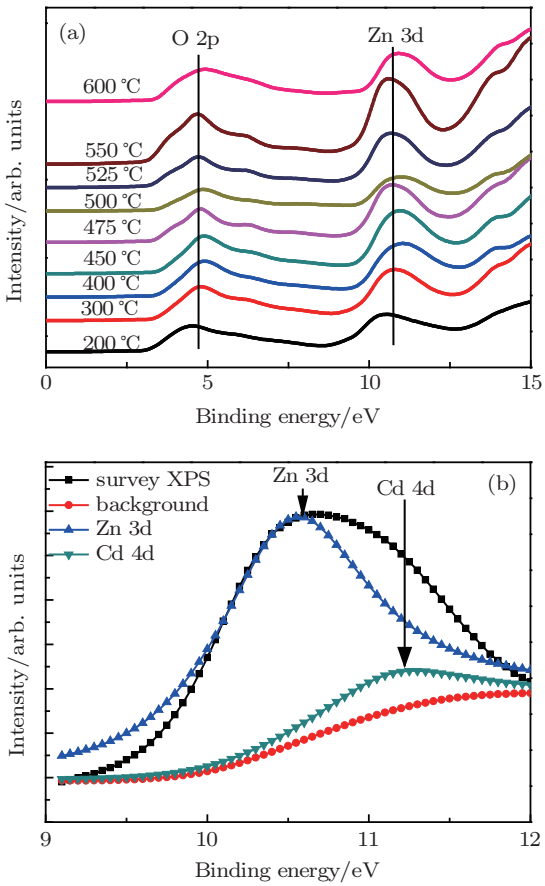


Fig. 4. (color online) (a) UPS-He I spectra of ZnCdO at different temperatures, (b) UPS detailed spectra of Zn 3d and Cd 4d at 525 °C.

The XRD patterns of $Zn_{1-x}Cd_xO$ film $x = (0.047 \pm 0.003)$ grown on c-plane sapphire substrate are shown in Fig. 5. The $2\theta \sim \theta$ scans of $Zn_{0.95}Cd_{0.05}O$ films show only the peak (0002) from wurtzite $Zn_{0.95}Cd_{0.05}O$ phase and a peak from the c-plane Al_2O_3 substrate. Especially, no indication of any rocksalt phase related to segregated CdO within the layers could be detected.[20] The strongest peak can be assigned to crystalline ZnCdO with lattice constants of $a = 3.22$ and $c = 5.21$, indicating that lattice constants are in accordance with RHEED data. It is observed in the inset of Fig. 5 that the root mean square (RMS) roughness over a scan area of 1 μm×1 μm is 0.64 nm.

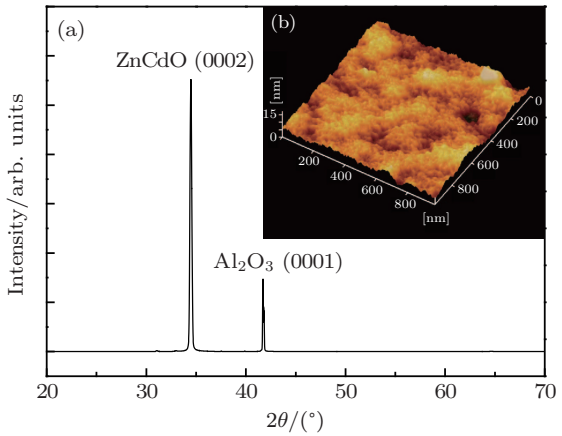


Fig. 5. (color online) XRD patterns and,with the inset showing AFM image of the ZnCdO at 500 °C.

Optical transmission spectra of ZnCdO films with five representative substrate temperatures are shown in Fig. 6. The transmission spectra of the thin films exhibit the abrupt decrease below about 400 nm. The absorption edges of ZnCdO thin films are at a wavelength of about 375 nm. Above about 470 nm, the thin film shows excellent optical transmission. The thin film deposited at 200 °C shows a lower optical transmittance in a range of 410 nm–468 nm. The band gap energy of $Zn_{1-x}Cd_xO$ films at the room temperature is plotted as a function of temperature in the inset of Fig. 6. The optical band gap E_g of the films is extracted from transmission spectra by plotting α^2 (the optical absorption coefficient) versus $h\upsilon$ and extrapolating the linear portion of this plot to the temperature axis. The band gap extending to 2.84 eV could be achieved by incorporating Cd with 29.6 at.%.

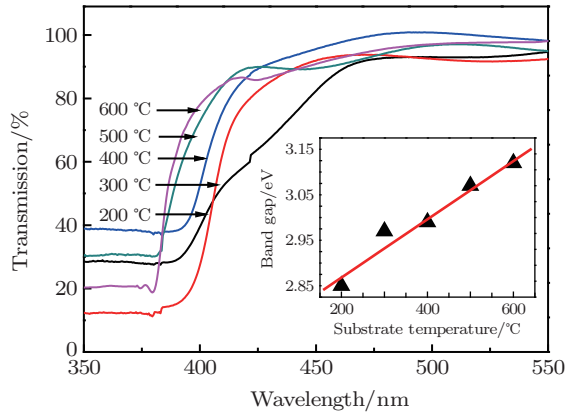


Fig. 6. (color online) Variations of transmission of ZnCdO films with wavelength at different temperatures, with the inset showing the variation of band gap energy with different substrate temperatures.

As a function of temperature, the electrical conductivity of the $Zn_{0.95}Cd_{0.05}O$ film is presented in Fig. 7. Four electrodes are used in the text. With increasing the temperature from 300 K to 500 K, the conductivity of $Zn_{0.95}Cd_{0.05}O$ film increases significantly. The resistivity of $Zn_{0.95}Cd_{0.05}O$ film is about 1.07×10^6 Ω·cm at room temperature. The relevant theory is as follows:

$$n = \left(\frac{N_D N_C}{g_D}\right)^{1/2} \exp -\frac{\varepsilon_D}{2k_B T}, \tag{3}$$

$$\varepsilon_D = E_C - E_D, \tag{4}$$

$$\sigma = ne\mu, \tag{5}$$

where n is the concentration of electrons, N_D is the concentration of donor impurities, g_D is the spin degeneracy, N_C is the concentration of electrons in conduction band, ε_D is the ionization energy of impurities, E_C is the conduction band level, E_D is the impurity level, σ is the conductivity, and μ is the carrier mobility. In a range from 300 K to 500 K, we consider N_D, N_C, and μ to be constants. The calculated ionization energy of impurities is 0.03 eV of $Zn0_{.95}Cd_{0.05}O$ film. When the deposited temperature increases, ionization energy of impurities decreases. The oxygen deficiency of ZnCdO film could be contributed by the donor level.

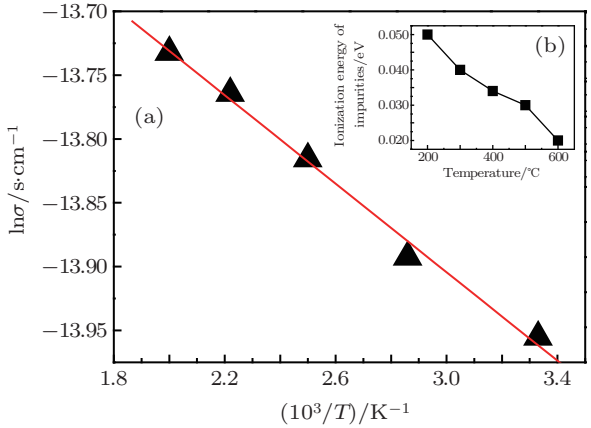


Fig. 7. (color online) Conductances of $Zn0_{.95}Cd_{0.05}O$ film at different temperatures, and the inset shows the variation of ionization energy of impurities of ZnCdO film with different temperatures.

4. Conclusions

In this study, $Zn_{1-x}Cd_xO$ layers are grown on sapphire substrates by LMBE. The best deposition temperature for ZnCdO film is 500 °C with the Cd content about 5%. The RHEED patterns gives a lattice constant of 3.20 Å. This relationship corresponds to a 30°-in-plane rotation of the film with respect to the substrate. The maximum Cd content of ZnCdO film grown at low substrate temperatures goes up to about 29.6 at.%, which is close to that of the target. The Cd percentage and the band gap of the ZnCdO film are both tunable through controlling the substrate temperature. *In situ* XPS results reveal that the energetic distance between $3Cd_{3/2}$ and $3Cd_{5/2}$ amounts to 6.7 eV. The peaks in a binding energy range of 3.0 eV–7.0 eV belong to the valence band of ZnCdO, contributed by O2p state mainly. RMS roughness of $Zn0_{.95}Cd_{0.05}O$ over a scan area of 1 μm×1 μm is 0.64 nm. Finally, the optical transmission spectra of the thin film show excellent optical transmittance above 400 nm.

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