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Temperature-dependent Hall and photoluminescence evidence for conduction-band edge shift induced by alloying ZnO with magnesium

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This work discusses the effect of conduction-band edge shift induced by alloying ZnO with magnesium. Temperature-dependent Hall and temperature-dependent photoluminescence measurements are used to characterize the epitaxial $Zn_{1-x}Mg_xO$ thin films grown on (111) Si using intervening epitaxial Lu_2O_3 buffer layers, which prove that the addition of Mg in ZnO shifts the conduction-band edge to higher energy, thus increasing the activation energy of the defect donor states and reducing the *n*-type background carrier concentration. © *2009 American Institute of Physics*. [doi:10.1063/1.3236771]

Due to its wide direct band gap of 3.37 eV and large room-temperature exciton binding energy of 60 meV, ZnO is considered as a promising material for short wavelength optoelectronic devices, such as blue-ultraviolet light-emitting diodes (LEDs) and laser diodes.[1,2] Recently, through considerable effort worldwide, investigations of *p*-type ZnO and ZnO-based LEDs has proceeded at a rapid pace.[3–5] In the mean time, band gap engineering is also needed to realize high-performance ZnO-based devices. The ternary alloy semiconductor, $Zn_{1-x}Mg_xO$, is considered one of the best candidates for increasing the band gap energy of ZnO. Thus, more effort should be directed toward the study of $Zn_{1-x}Mg_xO$ thin films. So far, most previous work has focused on $Zn_{1-x}Mg_xO$ doping[6–9] and quantum confinement effects in $Zn_{1-x}Mg_xO/ZnO$ quantum wells or superlattices.[10–12] There are only a few reports on the band shift due to adding Mg in ZnO.[13] To this work, we consider the band shift induced by alloying ZnO with Mg, focusing on the conduction-band edge. Temperature-dependent photoluminescence (PL) and temperature-dependent Hall measurements are used to characterize epitaxial $Zn_{1-x}Mg_xO$ thin films.

The $Zn_{1-x}Mg_xO$ films are grown on (111) Si substrates by pulsed laser deposition using a target of high purity ZnO–MgO ceramic disk with Mg content of 10 at. %. A KrF excimer laser (248 nm) is employed to ablate the target. Details of the growth process are described elsewhere.[14] In order to obtain high crystalline quality and a flatter surface, Lu_2O_3 buffer layers with a thickness of 30 nm are grown on (111) Si at 700 °C by reactive molecular-beam epitaxy. Detailed growth conditions are given in Ref. 15. A schematic illustration of the $Zn_{1-x}Mg_xO$ film is shown in Fig. 1.

The Mg content in the $Zn_{1-x}Mg_xO$ films is determined by Rutherford backscattering spectroscopy (RBS). The optical and electrical properties of the $Zn_{1-x}Mg_xO$ films are investigated by temperature-dependent PL and temperature-dependent Hall measurements. For comparison, the optical and electrical properties of pure ZnO films grown on (111) $Lu_2O_3/(111)$ Si substrates are also investigated.

RBS shows a Mg content of 9.7 at. % uniformly distributed in the film. Henceforth the films grown using this target will be referred to as $Zn_{0.9}Mg_{0.1}O$. Well resolved low-temperature PL spectrum is obtained in $Zn_{0.9}Mg_{0.1}O$ film, as shown in Fig. 2. This indicates the $Zn_{0.9}Mg_{0.1}O$ films grown on (111) $Lu_2O_3/(111)$ Si have good optical properties. In addition, all the PL peaks show a blueshift compared with those of pure ZnO film, which confirms that the addition of Mg in ZnO increases the fundamental band gap energy of ZnO. Based on our previous analysis, each peak has been assigned.[14] The strongest PL peaks, at 3.558 and 3.578 eV, are assigned to neutral donor bound exciton (D^0X) and ionized donor bound exciton transitions (D^+X). On the high-energy side of D^+X, a shoulder at 3.593 eV, is identified as the ground state emission of A free exciton (FX_A). On the low-energy side of D^0X, the first two peaks are assigned to FX longitudinal optical (LO) phonon replicas. The remaining two peaks have not yet been assigned.

Figure 2 also shows the near-band-edge (NBE) spectra from 10 to 300 K. As shown in Fig. 2, D^0X is dominant, with a shoulder of FX at 10 K. From 10 to 300 K, an obvious temperature-dependent redshift of D^0X and FX is observed.

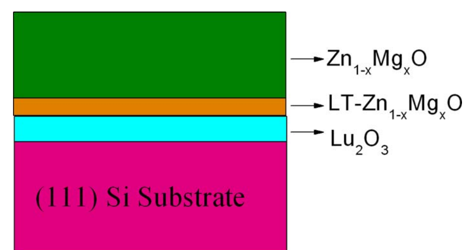

FIG. 1. (Color online) A schematic of an expitaxial $Zn_{1-x}Mg_xO$ film grown on a (111) Si substrate with an (111) Lu_2O_3 buffer layer.

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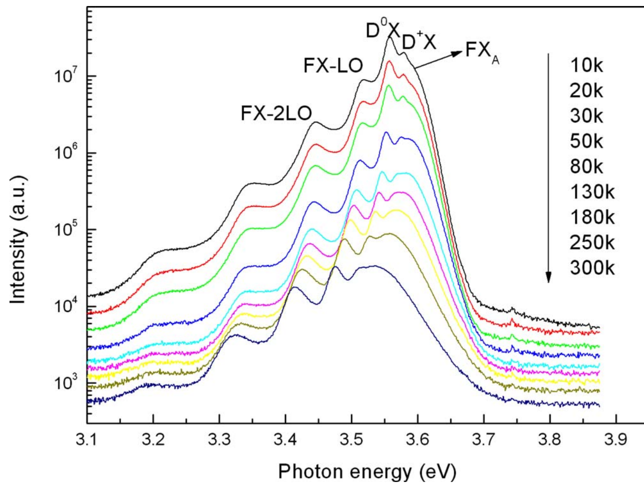

FIG. 2. (Color online) Temperature-dependent PL spectra of NBE emissions of $Zn_{0.9}Mg_{0.1}O$ thin film grown on (111) Lu_2O_3/(111) Si substrate.

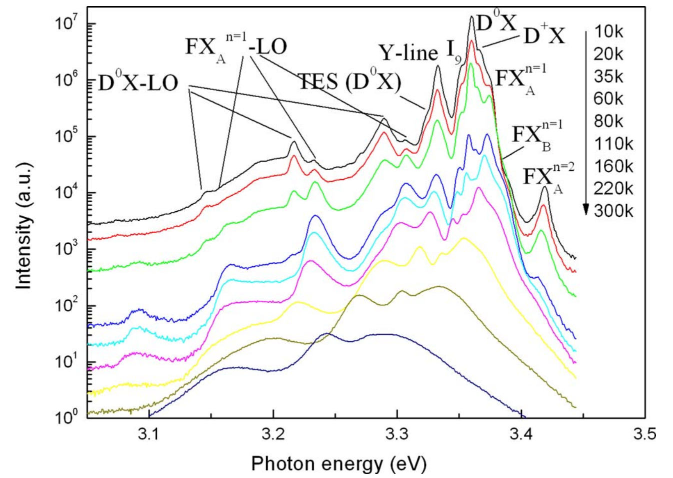

FIG. 3. (Color online) Temperature-dependent PL spectra of pure ZnO film grown on (111) Lu_2O_3/(111) Si substrate.

As the temperature increases, D^0X gives way to FX, and FX becomes more and more evident. This clearly suggests that D^0X emission gives way to FX emission at elevated temperatures due to the thermal ionization effect, which is also observed in pure ZnO films. As shown below, for pure ZnO films, as the temperature further increases, D^0X disappears, and FX becomes dominant. For the $Zn_{0.9}Mg_{0.1}O$ film, on the other hand, D^0X persists even at room temperature.

For FX emission, the energy, $E_{FX}(T)$, can be described as

$$E_{FX}(T) = E_g(T) - E_{ex}, \tag{1}$$

and the temperature-dependent band gap energy $[E_g(T)]$ is related to the temperature by the following equation:[16]

$$E_g(T) = E_g(0) - \alpha T^2/(T+\beta), \tag{2}$$

where E_g (0) is the band gap energy at 0 K, α and β are constants, T is the temperature, and E_{ex} is the free exciton binding energy (60 meV). Also, the D^0X energy $[E_{DX}(T)]$ may be simply expressed as

$$E_{DX}(T) = E_{FX}(T) - E_{loc}, \tag{3}$$

where E_{loc} is the bound exciton localization energy. Curve fitting using Eqs. (1)–(3) (data not shown) gives $E_{loc}(Zn_{0.9}Mg_{0.1}O) = 35$ meV. This value is bigger than k_BT at room temperature ($k_BT = 26$ meV), where k_B is Boltzmann's constant. Therefore, D^0X persists even at room temperature.

For comparison, temperature-dependent PL spectra of pure ZnO films grown on (111) Lu_2O_3/(111) Si substrates were also measured, as shown in Fig. 3. Each peak in the PL spectrum at 10 K has been assigned.[17] The strongest peaks, at 3.360 and 3.366 eV, are assigned to D^0X and D^+X or I_2.[18] On the high-energy side of these peaks, three peaks/shoulders at 3.375, 3.385, and 3.419 eV are identified as the ground state emissions of A and B free excitons ($FX_A^{n=1}$, $FX_B^{n=1}$) and the first excited state of the A free exciton ($FX_A^{n=2}$), respectively.[19] On the low-energy side of D^0X, a shoulder at 3.354 eV, which also has excitonic nature, could be the I_9 transition line.[18] A sharp transition at 3.333 eV is usually assigned to an exciton bound to structural defects such as Y-line defects.[18] Another shoulder at 3.325 eV is identified as the two-electron satellite transition of D^0X.[18] Other lines are LO phonon replicas, separated by 71–73 meV,[19] and associated with free and bound excitons. A similar analysis to that above has been used for pure ZnO films, which gives $E_{loc}(ZnO) = 15$ meV, which is much smaller than 35 meV, found above for $E_{loc}(Zn_{0.9}Mg_{0.1}O)$.

The Haynes factor (β), defined as[20]

$$\beta = E_{loc}/E_D, \tag{4}$$

for n-type, is widely accepted as a constant of 0.3 between the localization energy and the donor binding energy E_D.[18] Based on this value, $E_D(Zn_{0.9}Mg_{0.1}O)$ is derived to be 116.7 meV, whereas E_D (ZnO) is derived to be 50 meV. Compared with the two values of the donor binding energy of $Zn_{0.9}Mg_{0.1}O$ and ZnO, the $Zn_{0.9}Mg_{0.1}O$ donor level is deeper than that of ZnO.

Table I compares the results of Hall measurements made using the van der Pauw four-point configuration at room temperature. As shown in Table I, the $Zn_{0.9}Mg_{0.1}O$ film has a resistivity of 4.18 Ω cm, a Hall mobility of 17 cm^2/V s, and an electron concentration of 8.8×10^{16} cm^{-3}, while the ZnO film has a resistivity of 0.31 Ω cm, a Hall mobility of 80 cm^2/V s, and an electron concentration of 2.5×10^{17} cm^{-3}. The difference of the Hall results is attributed to alloying Mg in ZnO, which may be explained as follows. The addition of Mg in ZnO shifts the conduction-band edge to higher energy and increases the activation energy of the defect donor states, thus resulting in lower electron concentration and higher resistivity. At the same time, alloying Mg in ZnO induces a larger population of structural distortion, which consequently results in a decrease of the mobility.

The temperature-dependent Hall data of the $Zn_{0.9}Mg_{0.1}O$ film is shown in Fig. 4. The electron concentration exhibits a two order-of-magnitude change above 170 K. This abrupt increase in electron concentration with temperature indicates

TABLE I. Electrical properties of $Zn_{0.9}Mg_{0.1}O$ and ZnO thin films.

Sample	Resistivity (Ω cm)	Hall mobility ($cm^2\ V^{-1}\ s^{-1}$)	Carrier concentration (cm^{-3})	Carrier type
$Zn_{0.9}Mg_{0.1}O$	4.18	17	8.8×10^{16}	n
ZnO	0.31	80	2.5×10^{17}	n

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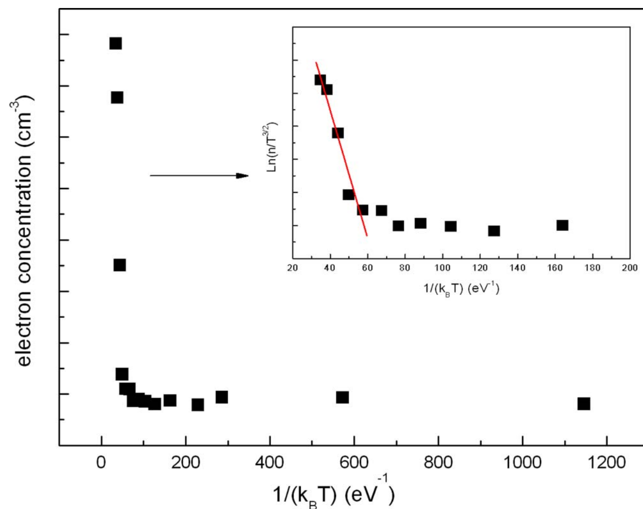

FIG. 4. (Color online) Temperature dependence of the electron concentration for $Zn_{0.9}Mg_{0.1}O$ film. The inset shows a plot of $\ln(n/T^{3/2})-1/(k_BT)$ from 170 to 330 K. The slope gives a thermal activation energy of 97 ± 13 meV.

that above 170 K, defect donors are gradually activated. As shown in the inset of Fig. 4, the donor activation energy is estimated to be 97 ± 13 meV, derived by using the relation

$$n \propto T^{3/2} \exp[-E_D/(K_BT)].$$

This value of the thermal activation energy E_D is in good agreement with the optical ionization energy $E_D(Zn_{0.9}Mg_{0.1}O)$, which is derived to be 116.7 meV by temperature-dependent PL spectra. A similar analysis has been used for pure ZnO film (data not shown), and the thermal activation energy is estimated to be 42 meV, which is in good agreement with our PL result.

It is well known that the addition of Mg in ZnO increases the band gap of ZnO. However, the effect of band shift by alloying Mg in ZnO has not been widely studied, which is due to relatively poor quality of $Zn_{1-x}Mg_xO$ films. As a result, there are few reports on the band shift induced by alloying ZnO with Mg. Recently, it is interesting that *p*-type $Zn_{1-x}Mg_xO$ thin films have been obtained through doping acceptor dopants such as nitrogen,[6] phosphorous,[7] antimony,[8] lithium[9] and so on. In that case, most group suggest that the easier realization of *p*-type $Zn_{1-x}Mg_xO$ compared with ZnO is attributed to the effect of alloying Mg in ZnO, which moves the conduction-band edge up in energy and potentially away from the shallow donor states, thus increasing the activation energy of the defect donors and reducing the *n*-type background carrier concentration. Although the suggestion seems reasonable, there is still no experimental evidence to prove it. Consequently, experimental evidence for the band shift induced by alloying ZnO with Mg is still rare. Considering our analysis measured by temperature-dependent PL and temperature-dependent Hall, we conclude that the addition of Mg in ZnO increases the band gap of ZnO, and shifts the conduction-band edge to higher energy, thus increasing the activation energy of the defect donor states and reducing the *n*-type background carrier concentration. We hope that this study will shed light on research on the band shift induced by alloying ZnO with Mg.

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