Optical properties of Zn$_{1-x}$Mn$_x$O thin films grown by molecular beam epitaxy

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Zn$_{1-x}$Mn$_x$O ($x=0–0.061$) thin films were grown by molecular beam epitaxy (MBE) system. Transmission shows an increase of the band gap with the increasing Mn concentration. Resonant Raman scattering (RRS) spectra showed 11 longitudinal optical phonon lines for the Zn$_{1-x}$Mn$_x$O samples. For the Zn$_{0.997}$Mn$_{0.003}$O sample, circular polarization degree of 9% was observed at magnetic field $B=5$ T. The dependence of circular polarization rate on the magnetic field intensity exhibits Brillouin type para-magnetism.

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1. Introduction

Zn$_{1-x}$Mn$_x$O was theoretically predicted [1] and experimentally observed [2] to exhibit ferromagnetism at room temperature. Spin dependent tunneling properties were observed in the metal–oxide-semiconductor diode consisting of ferromagnetic Zn$_{1-x}$Mn$_x$O nanocrystals [3]. However, there was no ferromagnetism observed for the Zn$_{1-x}$Mn$_x$O thin films grown by pulsed laser ablation and rf magnetron sputtering methods [4]. Mixed magnetic phases (paramagnetic and ferromagnetic) were reported for the Zn$_{1-x}$Mn$_x$O nanostructures synthesized by chemical vapor deposition [5]. This controversy of paramagnetism or ferromagnetism in Zn$_{1-x}$Mn$_x$O motivates intensive studies of magnetism in ZnO related materials in recent years [6,7]. In this study, Zn$_{1-x}$Mn$_x$O thin films were grown by plasma-assisted MBE. The magneto-optical properties were investigated to study the magnetism of Zn$_{1-x}$Mn$_x$O thin films and to explore the potential application of this material in the spintronic devices.

2. Experiments

Zn$_{1-x}$Mn$_x$O thin film was grown on c-plane Al$_2$O$_3$ substrate by a SVT Associates MBE system equipped with conventional effusion cells for evaporation of elemental Zn (6N), Mg (6N), and Mn (5N). Oxygen (5N) flow rate of 0.6 SCCM with plasma power 250 W is supplied via a rf-plasma source after additional gas purification. The substrates were degreased in acetone, methanol, and then chemically etched in H$_2$SO$_4$:H$_3$PO$_4$:H$_2$O$_2$:H$_2$O = 3:1 at 160 °C for 15 min followed by deionized water rinse and spin drying. Before growth, the substrates were desorbed at 850 °C and treated in oxygen plasma, which is expected to produce an oxygen terminated Al$_2$O$_3$ surface. In order to reduce the lattice mismatch, MgO was grown at 650 °C as a buffer layer. Because the lattice mismatch between the MgO and Al$_2$O$_3$ is 8%, that is lower than that between ZnO and Al$_2$O$_3$ (18%) [8]. A 325 nm He–Cd laser was used as the excitation source to obtain the PL and RRS spectra and a 800 W xenon lamp was the light source for the transmittance measurements. The RRS, PL and transmittance spectra were analyzed using a 0.55 m single-grating spectrometer and photomultiplier tube.

3. Results and discussion

Fig. 1(a) shows room temperature transmittance spectra of Zn$_{1-x}$Mn$_x$O thin films with Mn concentration x = 0, 0.009, 0.030 and 0.061. The absorption edge energy increasing with Mn concentration can be observed. Fig. 1(b) shows the absorption edge energy of the Zn$_{1-x}$Mn$_x$O versus Mn concentration. The blue shift of the absorption energy is due to MnO having a larger band gap than ZnO [9]. The shift of the absorption edge can be expressed by the following equation.

$$E(x) = 3.337 + 3.056x \text{ (eV)}$$  

The experimental results are in good agreement with reference [9]. Furthermore, the broadening of the absorption edge increases with the Mn concentration. The broadening is mainly due to the increasing disorder with increasing Mn concentration in Zn$_{1-x}$Mn$_x$O. There are also obvious mid-gap absorption around 3 eV for higher
Mn concentration samples. This effect has been ascribed to the d–d transitions of the Mn$^{2+}$ ion [10].

Fig. 2 shows low temperature (10 K) resonant Raman scattering (RRS) spectra of ZnO and Zn$_{0.97}$Mn$_{0.03}$O thin films with the He–Cd laser ($\lambda = 325$ nm) excitation. RRS experiment is performed under the excitation laser energy higher than the band gap, and the incident photon energy will be in resonance with the electronic interband transition. The peak at 578 cm$^{-1}$ is the first-order longitudinal optical (LO) phonon mode [11], in which both O and Zn atoms vibrate in the same direction. The weak peak around 457 cm$^{-1}$ is ascribed to the $E_{2}$ (high) mode. Compared with 440 cm$^{-1}$ in bulk ZnO single crystal [11], the frequency of the $E_{2}$ (high) mode in our sample is slightly larger, it is mainly due to strain effect in the thin film. Under RRS condition, some intense peaks at frequency positions of approximately integer times 578 cm$^{-1}$ contribute to the nth-order LO phonon scattering processes. These are intense LO phonon lines because of the Fröhlich interaction, which is the interaction between electrons and the longitudinal electrical field induced by the LO phonons [12]. In addition, there are also some relatively weak peaks at frequency positions next to these LO phonon modes. Considering the frequency positions of these peaks, they are probably caused by the combination of $E_{2}$ (high) mode and multiple LO phonon scattering.

From the RRS spectra, we find 5 and 11 LO phonon modes for ZnO and Zn$_{0.97}$Mn$_{0.03}$O samples, respectively. In previous studies [13], Scott et al. reported that the LO phonon numbers ($n$) in RRS spectra varies proportionally with the electron–phonon coupling coefficient ($\alpha$), which is given as the ratio of the Fröhlich interaction energy to the LO phonon energy. They also predicted the number of LO phonon modes in ZnO is more than $n=9$ in CdS. However, they only found $n=8$ in their ZnO sample. From our results, we could not find LO phonon lines for $n\geq 5$ in ZnO due to the strong near band edge PL emission. However, for Zn$_{0.97}$Mn$_{0.03}$O, the near band edge emission is weak and due to the large electron–phonon coupling coefficient $\alpha=0.9$ (is assumed to be the same as ZnO), the observation of large amount of LO phonon lines ($n=11$) in RRS spectra can be understood.

Fig. 3 shows the RRS spectra of Zn$_{1-x}$Mn$_x$O ($x=0.003–0.030$) thin films. Besides some intense LO phonon lines, there is an extra peak at 3632 cm$^{-1}$ for Zn$_{0.97}$Mn$_{0.03}$O sample. This peak is ascribed to the neutral donor bound exciton (D$^0$$\chi$) emission. As shown in the spectra, the LO phonon mode intensity at the frequency position of around 3500 cm$^{-1}$, which is assigned to the sixth-order LO phonon mode, is always the largest in each of
Zn$_{1-x}$Mn$_x$O samples, and the intensity decreases with increasing Mn concentration. The behavior of intensity variation is mainly related to the band gap position, and it can be explained by using the Raman cross section for the nth-order LO phonon mode which is given as [14]

$$\sigma_n(\omega) = \mu^2 \sum_{j=0}^{n} \sum_{m=0}^{n} \left| \langle x,m | e | e \rangle \langle e,m | x,j \rangle \right|^2 \exp \left( -\frac{\hbar \omega_{LO}}{k_B T} \right)$$

(2)

where $\mu$ is the electronic transition dipole moment, $\hbar \omega$ is the electronic transition energy. $\hbar \omega_{LO}$ and $\hbar \omega_{LO}$ are the energies of the incident photon and the LO phonon, respectively. $T$ is the homogeneous line width. $\langle x,m | e | e \rangle$ and $\langle e,m | x,j \rangle$ are the $(n+j)$th-order and $j$th-order LO phonon states in the electronic ground state, respectively. $\langle e,m | x,j \rangle$ is the nth-order LO phonon state in the electronic excited $e$ state. $k_B$ is Boltzmann’s constant and $T$ is the temperature. From this equation, the nth-order LO phonon mode intensity will become larger if $\hbar \omega \approx \hbar \omega_{LO}$. The band gap of Zn$_{1-x}$Mn$_x$O shifts to higher energy when Mn concentration increases, and it tends to be away from the frequency position of around 3500 cm$^{-1}$. Therefore, the intensity of sixth-order LO phonon mode decreases.

To investigate the dependence of RRS intensity on the band gap energy, temperature dependent RRS spectra of Zn$_{0.997}$Mn$_{0.003}$O is shown in Fig. 4(a). At 10 K, the intensity of sixth-order LO phonon mode around 3500 cm$^{-1}$ is the largest. However, when the temperature increases to 160 K, the seventh-order LO phonon mode around 4100 cm$^{-1}$ becomes the largest in intensity. The behavior can be explained by considering the temperature dependence of the photoluminescence (PL). Fig. 4(b) shows the PL peak position of Zn$_{0.997}$Mn$_{0.003}$O as a function of the temperature, and the curve can be fitted by considering the Bose–Einstein statistical factor for phonons [15]

$$E(T) = E(0) \frac{2 \hbar \omega}{\exp(\hbar \omega / k_B T) - 1}$$

(3)

where $E(T)$ and $E(0)$ are the energies at $T$ K and 0 K, respectively, $\hbar \omega$ is the strength of the electron–phonon interaction, and $\hbar \omega$ is associated with the mean frequency of the phonons. From Fig. 4(a) and (b), the shift of PL position results in the LO phonon line intensity variation.

To summarize, multiple LO phonon scattering in RRS spectra can be explained by using the “cascade model” [16,17], the scattered photons will have energy $\hbar \omega \approx \hbar \omega_{LO} - \hbar \omega_{LO}$ or $\hbar \omega \approx \hbar \omega_{LO} - \hbar \omega_{LO}$. Moreover, by studying RRS spectra, we find that when the scattered photon energy is close to the band gap, the LO phonon intensity will be resonantly enhanced.

Fig. 5 shows the low temperature (10 K) PL spectra of Zn$_{0.997}$Mn$_{0.003}$O analyzed by ($\sigma_+$) and ($\sigma_-$) circular polarization at magnetic field $B=0$ and $B=5$ T. At $B=0$, no difference was observed between two circular polarization. The D$^0$X (at 3.356 and 3.363 eV) and RRS (at 3.306 and 3.378 eV) intensities for ($\sigma_+$) and ($\sigma_-$) components are approximately the same. However, at $B=5$ T, a slight difference is observed between the two circular
polarization components of the D0X. While the intensities of the two circular polarization components of the RRS remain the same. The degree of circular polarization can be defined as

\[ P = \frac{I_{s+} - I_{s-}}{I_{s+} + I_{s-}} \]  

where \( I_{s+} \) and \( I_{s-} \) are the intensities of the right and left circular polarization, respectively. For RRS, \( P = 0\) at \( B = 0 \) and 5 T. Whereas, for D0X emission, \( P = 0 \) at 0 T and \( P = 9\% \) at 5 T. The non-zero circular polarization is due to the energy splitting of the two spin components of the D0X, (electron \(-1/2\) and hole \(-3/2\)) and (electron \(+1/2\) and hole \(+3/2\)). Although, the energy separation is too small to be resolved, due the energy relaxation from the higher energy spin state to the lower energy spin state, \( P = 9\% \) is observed. The dependence of circular polarization on the magnetic field shows Brillouin-type para-magnetism. No hysteresis is observed. It implies that the Zn0.997Mn0.003O exhibits paramagnetism due sp–d exchange interaction between conduction band s electrons/valence band p electron and d electrons of the Mn atoms.

4. Conclusion

We have grown Zn1-xMnO (x=0–0.061) thin films by MBE. Transmission measurement shows an increase of the band gap with the increasing Mn concentration. From RRS spectra, we observe LO phonon lines up to 5 and 11 order for ZnO and ZnMnO samples, respectively. From the temperature dependent RRS experiment, we find the intensities of these LO phonon lines are sensitive to the band gap position. Low temperature PL spectra of Zn0.997Mn0.003O at magnetic field \( B = 0 \) T and 5 T were investigated to calculate the degrees of circular polarization of \( P = 0\% \) and 9\%, respectively.

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References