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High-pressure phase transitions in $Zn_{0.83}Mn_{0.17}Se$ thin film

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Abstract

The energy-dispersive X-ray-diffraction (EDXD) and Raman spectroscopy are used to study phase transitions of $Zn_{0.83}Mn_{0.17}Se$ thin film up to 17.5 and 16.1 GPa, respectively. The EDXD results show that possible zinc blende(B3) to sodium chloride phase(B1) structure transition for $Zn_{0.83}Mn_{0.17}Se$ thin film occurs at 10.0 GPa. The unloading run reveals a reversible phase transition existed in the $Zn_{0.83}Mn_{0.17}Se$ thin film. For micro-Raman spectra at ambient pressure, three Raman peaks are distinct as LO, TO, and Mn local modes in $Zn_{1-x}Mn_xSe$ bulk. As the pressure is increased to 10.9 GPa, metallization occurs, the LO and Mn local phonon peaks disappear while the two unidentified Raman peaks of TO mode are still observable above the metallization pressure till 17.5 GPa. The phase transition pressure P_t obtained from the results of micro-Raman spectra seems to be in good agreement with that obtained by EDXD measurements.

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The recent developments of diluted magnetic semiconductors (DMS) in crystal growth and particularly in molecular beam epitaxy (MBE) [1–3] and hot wall epitaxial growth [4] now allow zinc blende structure crystals of $Zn_{1-x}Mn_xSe$ to be grown on GaAs(100) wafer. As a result of the tunability of the lattice parameters, these materials are excellent candidates for growing quantum wells and superlattices [5]. The existence of magnetic interactions within quantum wells and superlattices may result in new effects related to low dimensional phenomena [6] and the large Zeeman splitting of the electronic bands. This fact allows the formation of quantum wells whose depth can easily be tuned by using a magnetic field [7]. It is also possible to obtain different spin superlattices with field-induced type transitions. But, the study of the lattice vibration of the DMS thin film under high-pressure is still absent. To our knowledge, this is the first characterization of $Zn_{1-x}Mn_xSe$ thin film by using high-pressure technical measurements.

The thickness of $Zn_{0.83}Mn_{0.17}Se$ thin film was about 7000 Å. It was grown by the EPI 620 molecular beam epitaxy (MBE) system on GaAs(100) substrate [8]. The GaAs(100) substrate was then removed by etching it in a mixed solution of

$$H_2O_2:NaOH:H_2O = 1:5:5$$

in gramme before the thin film can be used in the micro-Raman and energy-dispersive X-ray-diffrac-

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tion (EDXD) measurements. Experimental details of micro-Raman and EDXD measurements and the details in the data fitting of the equation of state (EOS) and the Jandel Scientific Peakfit computer programs were described earlier [9–14]. The Germanium energy dispersive detector was set in the position where the diffracted angle (θ) was changed to 6°. So, the relation of the energy of reflection, E, versus d-spacings, d, was $Ed = 59.317$ keV Å.

A series of spectra of substrate free $Zn_{0.83}Mn_{0.17}Se$ thin film for different loading run and the process of decompressing to ambient pressure are shown in Fig. 1. The standard identified pressure lines of internal gold (111), (200), (220), (311), and (222) and the escape peaks of B3(220) are also manifested in Fig. 1. The peak positions are read out by a peak search program provided by the VAX computer in the beam line X-17C of Brookhaven National Lab [11,12]. The

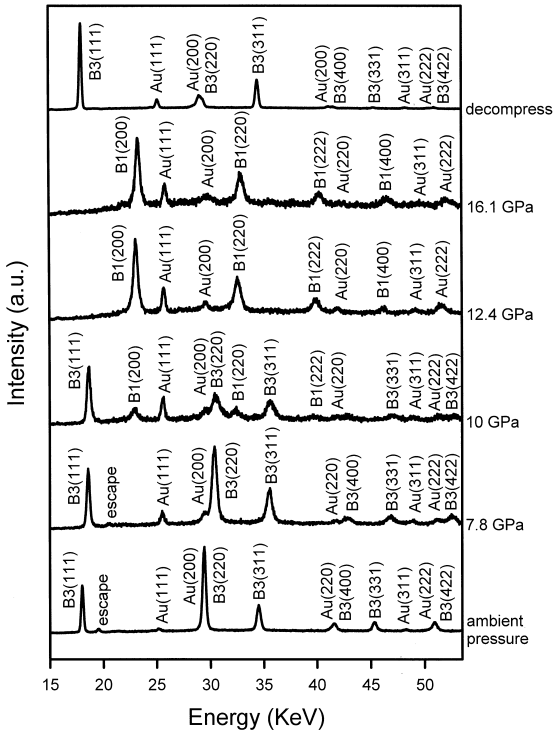

Fig. 1. A series spectra of $Zn_{0.83}Mn_{0.17}Se$ thin film at various pressure recorded in a loading run and process of decompressing to ambient pressure. The spectra contain the X-ray emission lines of the standard identified pressure lines of internal gold and the escape peaks of B3(220).

lattice parameter of $Zn_{0.83}Mn_{0.17}Se$ thin film is 5.704 ± 0.001 Å obtained from EDXD measurements for the loading run at ambient pressure. For the loading run at ambient pressure, Fig. 1 shows that there are six reflections (111), (220), (311), (400), (331), and (422) of B3 (zinc-blende, ZB) phase. By the relation $Ed = 59.317$ keV Å the d-spacings of those reflections appeared in Fig. 1 are 3.293, 2.016, 1.720, 1.426, 1.309 and 1.164 Å, respectively. Because the diffracted energy is very close to each other, the peaks Au(200) and B3(220); Au(220) and B3(400); and Au(222) and B3(422) respectively are overlapping together. No stress induced or GaAs diffraction peaks appeared in Fig. 1, which manifests that the removal of the GaAs substrate is able to establish a strain and substrate free experimental environment. At 7.8 GPa, all the peaks can be observed clearly. The fact that the B3 peaks appear at high energy side of the reflection of gold peaks exhibits that $Zn_{0.83}Mn_{0.17}Se$ thin film is more compressible than gold. When the pressure is increased to 10.0 GPa, the reflections (200), (220), and (222) of B1 (rock salt, RS) phase appear at high energy side of the reflections (111), (220), and (311) of B3 phase, respectively. While the reflection (400) of B3 (zinc-blende, ZB) phase disappears. The d-spacings at 10.0 GPa are 3.179, 1.944, 1.665, 1.261, and 1.124 Å for (111), (220), (311), (331), and (422) of B3 phase and the lattice parameter is 5.505 ± 0.001 Å. While the d-spacings at 10.0 GPa are 2.587, 1.830, and 1.492 Å for (200), (220), and (222) of B1 (rock salt, RS) phase and the lattice parameter is 5.173 ± 0.001 Å. The reflection (400) of B1 (rock salt, RS) phase appears at high energy side of the reflection (400) of B3 phase at 10.5 GPa. The reflections of the B3 phase of $Zn_{0.83}Mn_{0.17}Se$ disappear completely and only reflections of B1 phase appear apparently above 12.4 GPa. The transition pressure of B3 to B1 for $Zn_{0.83}Mn_{0.17}Se$ is assigned as 10.0 GPa. Actually, the exact phase transition pressure must exist between 10.0 to 12.4 GPa. The B1 reflections, (200), (220), (222), and (400) are found to exist up to 16.1 GPa. The unloading run reveals that $Zn_{0.83}Mn_{0.17}Se$ thin film has reversible pressure property.

The variations of the interplanar distances d_{hkl} (Å) for loading run of $Zn_{0.83}Mn_{0.17}Se$ thin film are shown in Fig. 2. All the interplanar distances de-

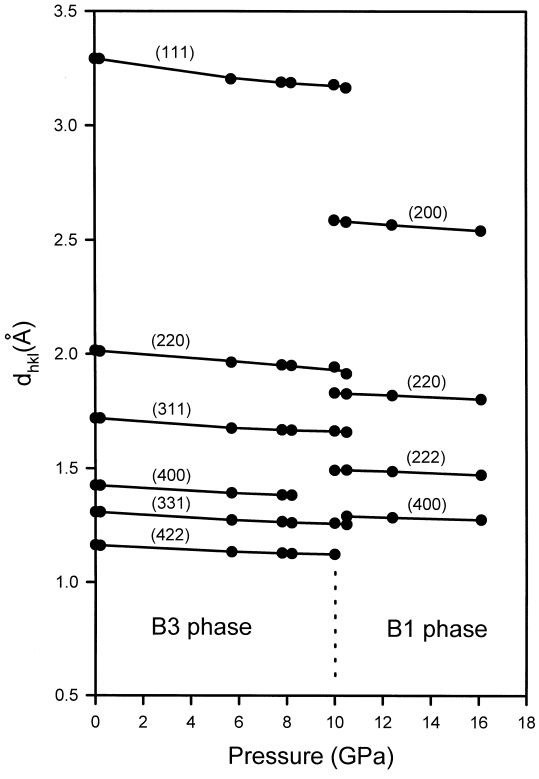

Fig. 2. The variation of d_{hkl} (Å) of $Zn_{0.83}Mn_{0.17}Se$ thin film with pressure (GPa) for the B3 and B1 phases.

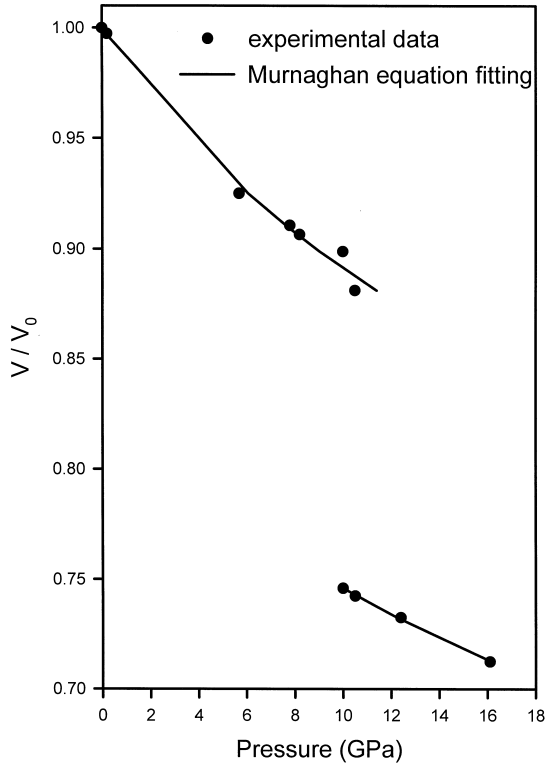

Fig. 3. The V / V_0 versus pressure and Murnaghan equation used to fit for the B3 and B1 phases of $Zn_{0.83}Mn_{0.17}Se$ thin film.

crease as the pressure is increased for both B3 and B1 phases. Fig. 3 shows the equation of state relations as a function of pressure for $Zn_{0.83}Mn_{0.17}Se$ thin film. V_0 is the volume at ambient pressure. The data for B3 and B1 phases are fitted to the Murnaghan equation by a fitting process of the previous reports [11,12,14]. The values of K_0, the isothermal bulk modulus at ambient pressure, and K_0', the pressure derivative of the isothermal bulk modulus evaluated at ambient pressure, of the Murnaghan equation for $Zn_{0.83}Mn_{0.17}Se$ thin film in the B3 and B1 phase transitions obtained from the fitting process are listed in Table 1. The values of K_0' values are consistent with the slops of *d*-spacings for below and above the phase transitions (B3 and B1 phases) in the loading run spectra. In general, the pressure derivative of B3 is larger than B1 phase in both bulk and thin film [11,12]. It also shows that $Zn_{0.83}Mn_{0.17}Se$ thin film in the pressure region (B1) above phase transition is less compressible than that in the pressure region (B3) below the phase transition. This result is the same as that exhibited in the case of bulk.

Raman spectra of $Zn_{0.83}Mn_{0.17}Se$ thin film at various pressure for different loading run are shown in Fig. 4. At ambient pressure, two peaks identified as the LO and weak TO phonons are observed at 255.5 and 207.3 cm^{-1}, respectively. This is consistent with the bulk work reported previously [10].

Table 1
The values of K_0 and K_0' for $Zn_{0.83}Mn_{0.17}Se$ thin film under and above phase transition (B3 and B1 phase) obtained from the fitting process by Xu et al. [14]. K_0 is the isothermal bulk modulus at zero pressure, and K_0' is the pressure derivative of the isothermal bulk modulus evaluated at zero pressure.

sample	phase	K_0 (GPa)	K_0'
$Zn_{0.83}Mn_{0.17}Se$ thin film	B3	62.77 ± 5.38	5.43 ± 2.56
	B1	67.18 ± 6.69	5.19 ± 2.67

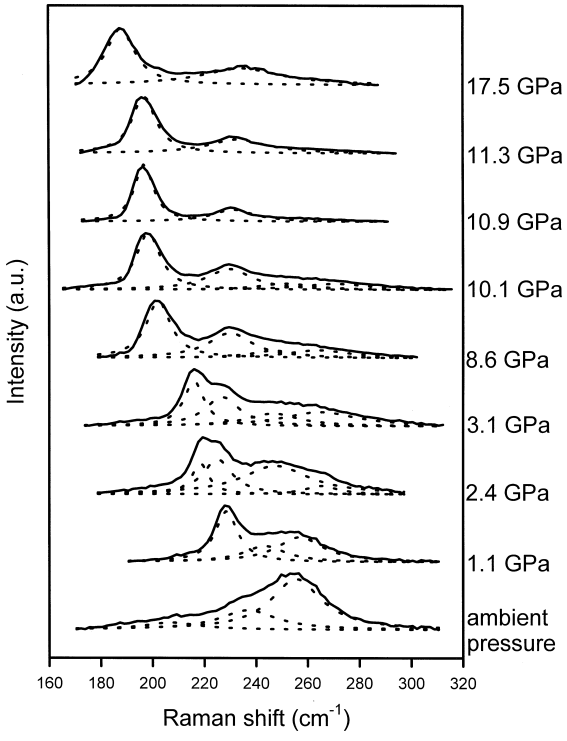

Fig. 4. Pressure dependence of phonon frequencies of $Zn_{0.83}Mn_{0.17}Se$ thin film. Note the lowest frequency component was softened at high pressure and was continuous to 17.5 GPa.

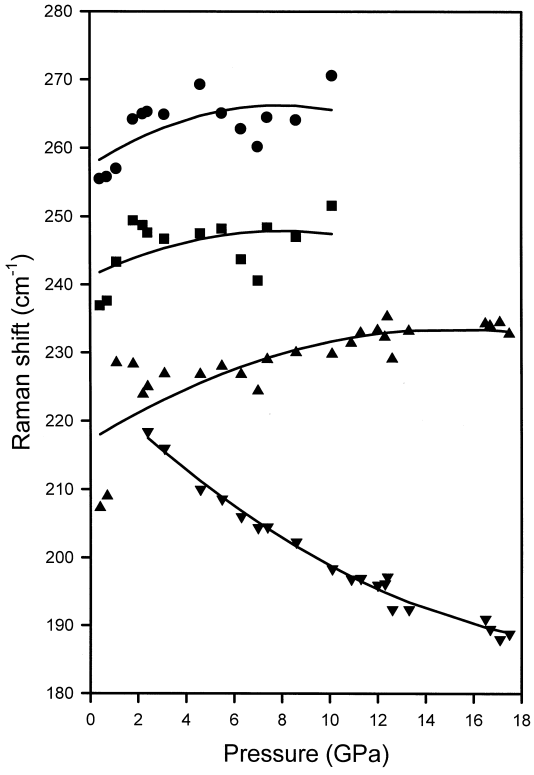

Fig. 5. Pressure dependence of Raman peaks in the $Zn_{0.83}Mn_{0.17}Se$ thin film. The solid lines are quadaratic polynomial fitting curves for $Zn_{0.83}Mn_{0.17}Se$ thin film.

Between these two peaks, a weak structure being able to be labelled through the Jandel Scientific Peakfit deconvolution process is attributed to the existence of the Mn local (impurity) phonon mode at 236.9 cm^{-1} [10,15,16]. Especially, there are none GaAs peaks in Fig. 1 [4,17], which agrees with the EDXD works. The Mn local phonon is caused from the local electric field resulting from the substituting Zn atom by the Mn atom [10,15,16]. The pressure effects on the LO and TO phonons exhibit similar blue shift behavior as the Mn local phonon [10,15,16]. As the pressure is increased to 2.4 GPa, one new mode which is labelled as TO split mode I appears at 218.4 cm^{-1}. This TO split mode I exhibits red shift and can be observed as the pressure is increased up to around 17.5 GPa [10]. As the pressure is increased further to 10.9 GPa, the semiconductor-metal transition of $Zn_{0.83}Mn_{0.17}Se$ thin film occurs, and both the LO and the Mn local modes disappear. Consistent with the EDXD works, the exact phase transition pressure must exist between 10.1 to 10.9 GPa. Hence, we may conclude that the measured results of semiconductor-metal transition pressure of $Zn_{0.83}Mn_{0.17}Se$ thin film obtained in EDXD and micro-Raman works are in good agreement. Below the metallization pressure, only one phase transition pressure can be observed. After the metallization pressure, only two TO peaks can be observed up to 17.5 GPa. The previous work of $Zn_{0.76}Mn_{0.24}Se$

Table 2
The quadratic polynomial fitting equation of the $Zn_{0.83}Mn_{0.17}Se$ thin film

Raman modes	Quadratic polynomial fitting equation
LO	$257.4 + 2.24p - 0.142p^2$
Mn local	$241.1 + 1.68p - 0.104p^2$
TO	$217.2 + 2.16p - 0.071p^2$
TO split (I)	$225.2 - 3.37p + 0.074p^2$

bulk [18] showed that three TO peaks can exist after the metallization pressure. We suggest that the absence of one TO peak in the thin film after the metallization transition is attributed to the lower dimensional behavior of the thin film. There are no structure transitions identified by experimental reports below metallization until now. Accroding to the theoretical works of Côté et al. for ZnSe [19] and Ahuji et al. and Nelmes et al. for CdTe [20,21]. We therefore attribute the appearance of the new phonon mode to the broken symmetry of the structure transformation. The splitting of TO phonon at 2.4 GPa could be also due to the structure transition as zinc-blende phase transforms into cinnabar phase [18].

The variation of the mode energies as a function of the pressure are shown in Fig. 5. The solid circle, solid square, solid triangle up, and solid triangle down symbols correspond to the LO, Mn local, TO and TO split Raman modes of $Zn_{0.83}Mn_{0.17}Se$ thin film, respectively. The relationships of the mode frequencies versus pressure of $Zn_{0.83}Mn_{0.17}Se$ thin film can be obtained by the quadratic polynomial fitting using the equations listed in Table 2, where ω_i is the wave number in cm^{-1} and p is the pressure in GPa. The effects of pressure on various Raman vibrational modes of $Zn_{0.83}Mn_{0.17}Se$ thin film at room temperature (298 K) are listed in Table 3. The Grüneisen parameter (γ_i) for a quasi-harmonic mode i of frequency ω_i was defined by Cardona et al. [22]. As a comparison with the previous works with bulk [10,23], some conclusions can be obtained: (i) the γ_{LO} value of $Zn_{0.83}Mn_{0.17}Se$ thin film is 0.546; (ii) the γ_{TO} value of $Zn_{0.83}Mn_{0.17}Se$ thin film is 0.624, and is larger than the γ_{LO} value; (iii) the ratio γ_{TO}/γ_{LO} for $Zn_{0.83}Mn_{0.17}Se$ thin film is 1.143. This manifests that $Zn_{0.83}Mn_{0.17}Se$ thin film also has higher ionicity from the Mn impurity as the previous works with bulk [10–12,23].

In summary, we have carried out high-pressure micro-Raman scattering and EDXD experiments on $Zn_{0.83}Mn_{0.17}Se$ thin film up to 17.5 and 16.1 GPa, respectively. The existence of the Mn element causes a reduction in the semiconductor-metal phase transition pressure that is in similar to the behavior of bulk. The disappearance of the LO and Mn local phonons is attributed to the metallization of the $Zn_{0.83}Mn_{0.17}Se$ thin film. Two components of visible TO phonon splitting in $Zn_{0.83}Mn_{0.17}Se$ thin film system were observed up to 17.5 GPa. The calculated Grüneisen parameter implied that $Zn_{0.83}Mn_{0.17}Se$ thin film has higher ionicity. Our EDXD data showed that the bulk modulus for $Zn_{0.83}Mn_{0.17}Se$ thin film was 62.77 ± 5.38 GPa before phase transition and the pressure derivative was 5.43 ± 2.56. We conclude that the measured results of the semiconductor-metal transition pressure of $Zn_{0.83}Mn_{0.17}Se$ thin film in EDXD and micro-Raman works are in good agreement with each other.

Table 3
Effect of pressure on various Raman vibrational modes of $Zn_{0.83}Mn_{0.17}Se$ thin film at room temperature (298K). The values of mode frequencies ω_i, pressure dependence $d\omega_i/dp$, mode Grüneisen parameter γ_i are extrapolated at ambient conditions

mode	ω_i (cm^{-1})	$d\omega_i/dp$ cm^{-1} GPa^{-1}	γ_i $[(\frac{K_0}{\omega_i})(\frac{d\omega_i}{dP})]$
LO	257.4	$2.24-0.142p$	0.546
Mn local	241.1	$1.68-0.104p$	0.437
TO	217.2	$2.16-0.071p$	0.624
TO split (I)	225.2	$-3.37+0.074p$	-0.939

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