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Chih-Ming Lin and Der-San Chuu

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Raman spectroscopy study of $Zn_{1-x}Mn_xSe$ thin films under high-pressure

Chih-Ming Lin[a)]
Department of Applied Science, National Hsinchu University of Education, Hsinchu 30014, Taiwan

Der-San Chuu
Department of Electro-Physics, National Chiao Tung University, Hsinchu, 300, Taiwan

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Raman spectroscopy was used to study phase transitions of substrate-free $Zn_{1-x}Mn_xSe$ thin films, $x=0.07$, 0.17, and 0.29, under high pressure up around 20.0 GPa at ambient temperature. One Raman mode, transverse optical split mode, was observed before metallization at 2.9 ± 1.0, 2.4 ± 0.8, and 2.1 ± 0.6 GPa for $Zn_{0.71}Mn_{0.29}Se$, $Zn_{0.83}Mn_{0.17}Se$, and $Zn_{0.93}Mn_{0.07}Se$ thin films, respectively. The semiconductor-metallic transition pressure for $Zn_{0.71}Mn_{0.29}Se$, $Zn_{0.83}Mn_{0.17}Se$, and $Zn_{0.93}Mn_{0.07}Se$ thin films was observed at 9.4 ± 0.4, 10.9 ± 0.6, and 11.7 ± 0.2 GPa, respectively. It was found that the relation of the ionicity and the reduction of the pressure in transition from semiconductor to metal phase for $Zn_{1-x}Mn_xSe$ thin films was not the same as that of bulk crystals. The percentage of the increasing of the Grüneison parameter of longitudinal optical mode for semiconductor to metal phase transition might be the important factor inherently related to the reduction of phase transition pressure for substrate-free $Zn_{1-x}Mn_xSe$ thin film systems. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2735679]

I. INTRODUCTION

Diluted magnetic semiconductors (DMS), especially for $Zn_{1-x}Mn_xSe$, are the materials in which transition metal elements are substituted by a fraction (x) of one to several tenths of a percent of cations in host semiconductors. For the studies of high pressure structural transition, a number of experiments have been performed to directly measure the dependence of the semiconductor-metal transition pressure, P_t, on Mn concentration x. Ves *et al.*[1] investigated the variation of P_t of $Zn_{1-x}Mn_xSe$ bulk crystals with the impurity concentration x of Mn. They concluded that the decreasing of the semiconductor-metal phase transition pressure was strongly dependent on the increasing of the Mn concentration. Maheswaranathan *et al.*[2] and Maheswaranathan and Sladek[3] indicated that the substitution of Mn makes the zinc blende or würtzite lattice less stable not only in CdMnTe and ZnMnSe, but also in all the other Zn- and Cd-based $A^{II}MnB^{VI}$ compounds. They found that Mn, but not Zn, weakens the zinc blende crystal structure and makes it less stable under the application of pressure. They suggested that in Mn, but not in Zn, 3*d* orbital hybridizes into the tetrahedral bonds because the 3*d* electrons are less tightly bound in Mn than in Zn. They also found that in Cd and Zn *d* levels do not hybrid with the sp^3 bonding orbital. Therefore, the cause of the reduction of the phase transition pressure was attributed to the hybridization of the Mn *d* orbital into the tetrahedral bonds in the Mn-ternary alloys and the tetrahedral structures of zinc blende and würtzite are sustained by the sp^3-hybridized with partially ionic covalent bonds. The valence electrons depopulate the sp^3 bonding states of the cation to make the tetrahedral bonds more ionic. Arora *et al.*[4] investigated the relationship of P_t vs x in the ternary system $Zn_{1-x}Mn_xSe$. They observed that the transition pressure did not manifest a strong dependence on the Mn concentration. Lin *et al.*[5] suggested that the effect of increasing the percentage of the reduction of volume change factor of ZnSe based ternary semiconductors with any kind of impurity ions may be the main reason to reduce the stability of the zinc blende phase under the application of pressure. However, no apparent effect of 3*d* electronic hybridization has been observed. On the other hand, the Raman scattering of the high pressure effects on transverse optical (TO) and longitudinal optical (LO) phonons studied by Arora *et al.*[4] showed that in $Zn_{1-x}Mn_xSe$ an intermediate phase, whose structure was not yet identified, precedes the rock salt phase in a comparatively low pressure range 2–4 GPa. To explore more deeply the reason of the reduction of the semiconductor-metal phase transition pressure of the ternary system $Zn_{1-x}Mn_xSe$, a more detailed investigation of the high pressure effect on $Zn_{1-x}Mn_xSe$ system is necessary. Among the aforementioned $Zn_{1-x}Mn_xSe$ systems, the previous works have only concentrated on the high pressure effects on the bulk matrices. There is an unavoidable creation of some level of micrograins, disorder, defects, oxidation, and intergrain boundaries in thin film for $Zn_{1-x}Mn_xSe$ material. Since the aforementioned effects are not able to be separated clearly, we thus consider a series of substrate-free $Zn_{1-x}Mn_xSe$ thin films.

In this work, we extend our previous study[6] to the investigation of the lattice vibration of the substrate-free $Zn_{1-x}Mn_xSe$ thin films by Raman measurements under high pressure. Our data of phase transition pressures are the direct observation in substrate-free $Zn_{1-x}Mn_xSe$ thin film system.

II. EXPERIMENT

The thickness of $Zn_{1-x}Mn_xSe$ thin films with $x=0.07$, 0.17, and 0.29, are around 7000 Å. They were grown by the EPI 620 molecular beam epitaxy system on GaAs(100) wa-

[a)]Author to whom correspondence should be addressed; electronic mail: cmlin@mail.nhcue.edu.tw

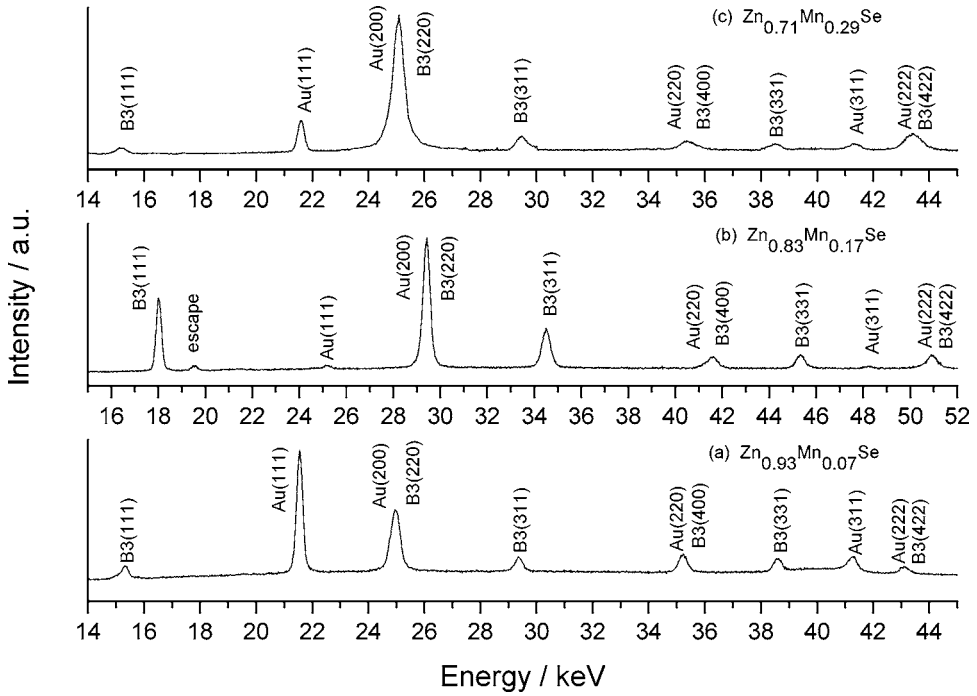

FIG. 1. A series of spectra of substrate-free $Zn_{1-x}Mn_xSe$ thin films at ambient pressure. There is only a B3 (zinc blende) phase, which also contains the standard identified pressure lines of internal gold.

fer. The sample preparation and the control of parameters for Raman measurements follow our previous work.[6] The films and ruby chips were sealed with the pressure transmitting medium (methanol-ethanol 4:1 fluid) in the sample chamber which was a hole of 130 μm in diameter and 50 μm in thickness drilled on the stainless steel 301 gasket as the same as previous work.[6] The pressure was calibrated by the fluorescence scale method.[7,8] Ruby fluorescence and Raman scattering measurements were performed in a TRIAX 550 micro-Raman system. The 5145 Å line with power of 0.6 W from the Spectra-Physics stabilite 2017 6.0 W argon ion laser was focused to about 5 μm on the sample surface. The backscattered signal was collected by a microscopic system and recorded with a Jobin–Yvon Spex spectrum one liquid nitrogen cooled charge coupled device detector. The recording time for each ruby fluorescence is of the order of 1 s, and Raman spectrum, 600 s. After the experiments, the spectra were processed to calculate the position, intensity, and the width at the half maximum under a Jandel Scientific Peakfit computer program as previous work.[6] The precision in the frequency determination was in the range of 1 cm^{-1}. The corresponding error of pressure values was within $\pm 0.1-0.2$ GPa at the highest pressure obtained because the good signal-to-noise ratio could be achieved in the system even for broad peaks below around 20 GPa. Energy-dispersive x-ray-diffraction (EDXD) measurement has been employed to characterize the structure phase of substrate-free $Zn_{1-x}Mn_xSe$ thin films at ambient pressure. The source of EDXD is the superconductor wiggler synchrotron beam line X17C of the National Synchrotron Light Source of Brookhaven National Laboratory, USA. The germanium energy dispersive detector was set in the position where the diffracted angle (θ) was changed to 6° for substrate-free $Zn_{0.83}Mn_{0.17}Se$ and 7° for $Zn_{0.93}Mn_{0.07}Se$ and $Zn_{0.71}Mn_{0.29}Se$, respectively. The relation of the energy of reflection, E, versus d spacings, d, was $Ed = 59.317$ and 50.866 keV Å for $\theta = 6°$ and 7°, respectively. Figure 1 shows the EDXD pattern of the substrate-free $Zn_{1-x}Mn_xSe$ thin films, (a), (b), and (c) are for $Zn_{0.93}Mn_{0.07}Se$, $Zn_{0.83}Mn_{0.17}Se$, and $Zn_{0.71}Mn_{0.29}Se$, respectively. One can note from Fig. 1 that the composition of the substrate-free $Zn_{1-x}Mn_xSe$ thin films is homogeneous. In Fig. 1, the B3 (zinc blende) phase but not the wurtzite phase can be observed. Especially, no mixture of zinc blende and wurtzite structures can be found for $x=0.29$ in our case not as those observed by Yoder-Short *et al.*[9] and Arora *et al.*'s works.[4]

III. RESULTS AND DISCUSSION

The pressure dependence of Raman scattering spectroscopy at ambient temperature for substrate-free $Zn_{1-x}Mn_xSe$ thin films, $x=0.07$ and 0.29, is shown in Figs. 2 and 3, respectively. Similar results of Raman works of substrate-free $Zn_{0.83}Mn_{0.17}Se$ thin film were reported in the previous work.[6] At ambient pressure, two peaks identified as LO and TO phonons were observed at 254.8 and 207.5 cm^{-1}, 255.8 and 208.4 cm^{-1} for substrate-free $Zn_{0.93}Mn_{0.07}Se$ and $Zn_{0.71}Mn_{0.29}Se$ thin films, respectively. Between these two peaks, a weak structure attributed to the Mn local (impurity) phonon mode can be labeled through the deconvolution process at 229.9 and 234.9 cm^{-1} for substrate-free $Zn_{0.93}Mn_{0.07}Se$ and $Zn_{0.71}Mn_{0.29}Se$, respectively. The labeled Mn local phonon mode is arisen from the introducing of the local electric field resulting from the substitution of Zn atom by Mn atom as bulks. At around 1.3 ± 0.2 GPa, for $x=0.07$ and 0.29, the Mn local mode becomes more intense at higher

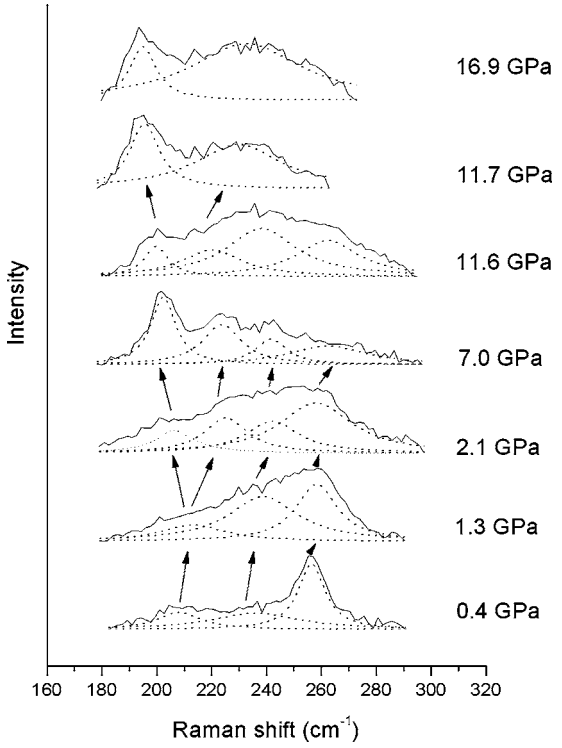

FIG. 2. Pressure dependence of phonon frequencies of substrate-free $Zn_{0.93}Mn_{0.07}Se$ thin film. Note the lowest frequency component is softened at high pressure and was continuous to 16.9±0.2 GPa.

pressure and the Raman shift energy is increased with the pressure. A split TO phonon mode starts to develop and it becomes very pronounced at 2.1±0.6 and 2.9±1.0 GPa for substrate-free $Zn_{0.93}Mn_{0.07}Se$ and $Zn_{0.71}Mn_{0.29}Se$ thin films,

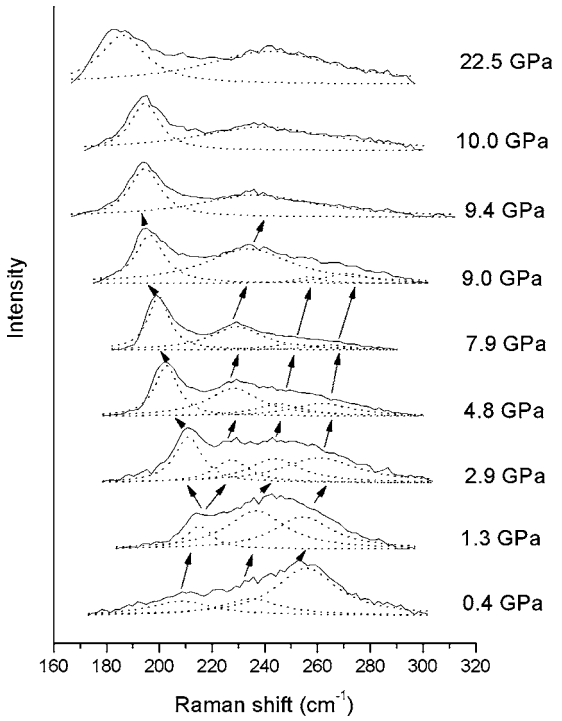

FIG. 3. Pressure dependence of phonon frequencies of substrate-free $Zn_{0.71}Mn_{0.29}Se$ thin film. Note the lowest frequency component is softened at high pressure and was continuous to 22.5±0.2 GPa.

TABLE I. Phase transition presents (including those of one phase) of substrate-free $Zn_{1-x}Mn_xSe$ thin films are listed and compared with ZnSe bulk.

Sample	One phase pressure (GPa): redshift	Metallization pressure (GPa)
ZnSe bulk	4.7±0.3	14.4±0.3
$Zn_{0.93}Mn_{0.07}Se$ thin film	2.1±0.6	11.7±0.2
$Zn_{0.83}Mn_{0.17}Se$ thin film	2.4±1.0	10.9±0.6
$Zn_{0.71}Mn_{0.29}Se$ thin film	2.9±0.8	9.4±0.4

respectively. The error bar of 0.4 and 0.8 GPa results from the difficulty of pressure tuning while the error of 0.2 GPa comes from the uncertainty of the pressure determination for substrate-free $Zn_{0.93}Mn_{0.07}Se$ and $Zn_{0.71}Mn_{0.29}Se$ thin films, respectively. Similar blueshift behavior as that of the Mn local phonon mode is exhibited in the pressure effect on the LO and TO phonon modes. One Raman mode, TO split mode, occurs before metallization at 2.1±0.6 and 2.9±1.0 GPa for substrate-free $Zn_{0.93}Mn_{0.07}Se$ and $Zn_{0.71}Mn_{0.29}Se$ thin films, respectively. This is similar to the case of substrate-free $Zn_{0.83}Mn_{0.17}Se$ film in which the TO split mode happens at 2.4±0.8 GPa. In the case of $Zn_{1-x}Mn_xSe$ bulk crystal, one more mode, the Mn impurity mode, was also observed.[10] Arora *et al.*[10] reported that the splitting of the impurity mode at 4.0 GPa is caused by the lowering of the crystal symmetry. However, if one refers to the study of the similar cubic structure of CdTe (Ref. 11) and HgTe,[12] one more phase (cinnabar for CdTe and HgTe) is observed before they undergo the structure transformation from the B3 phase to the B1 phase and is similar to our previous work on the bulk crystal of ZnSe DMS.[13] Therefore, it is reasonable to suspect that substrate-free $Zn_{1-x}Mn_xSe$ thin films might also undergo a similar structure transformation from the B3 phase to the cinnabar structure for x=0.07, 0.17, and 0.29 at around 2.1±0.6, 2.4±1.0, and 2.9±0.8 GPa, respectively. The TO split mode exhibits a redshift and can be observed as the pressure is increased up to around 16.9±0.2, 17.5±0.2, and 22.5±0.2 GPa, for substrate-free $Zn_{0.93}Mn_{0.07}Se$, $Zn_{0.83}Mn_{0.17}Se$, and $Zn_{0.71}Mn_{0.29}Se$ thin films, respectively. As the pressure was increased further to 11.7±0.2 and 9.4±0.4 GPa for substrate-free $Zn_{0.93}Mn_{0.07}Se$ and $Zn_{0.71}Mn_{0.29}Se$ thin films, respectively, which are the semiconductor-metal transition pressures for these two thin films, both LO and Mn local modes disappear.[6,13] The disappearance of the LO phonon and Mn local phonon modes can be understood as a semiconductor-metallic transition from the high pressure Raman spectroscopy measurements on the ZnSe bulk.[13] Two phase transition pressures of substrate-free $Zn_{1-x}Mn_xSe$ are listed in Table I. One can find that with 600 mW laser power at 514.5 nm and 600 s collecting time, the final Raman spectroscopy are still not good enough in diamond anvil cell (DAC) condition, especially compared with the results from other groups.[4,10] For vibrations of a crystal lattice, the intensity of the TO and LO branches depend upon the magnitude of the dipole moment created by the vibrational mode. The dimension of the

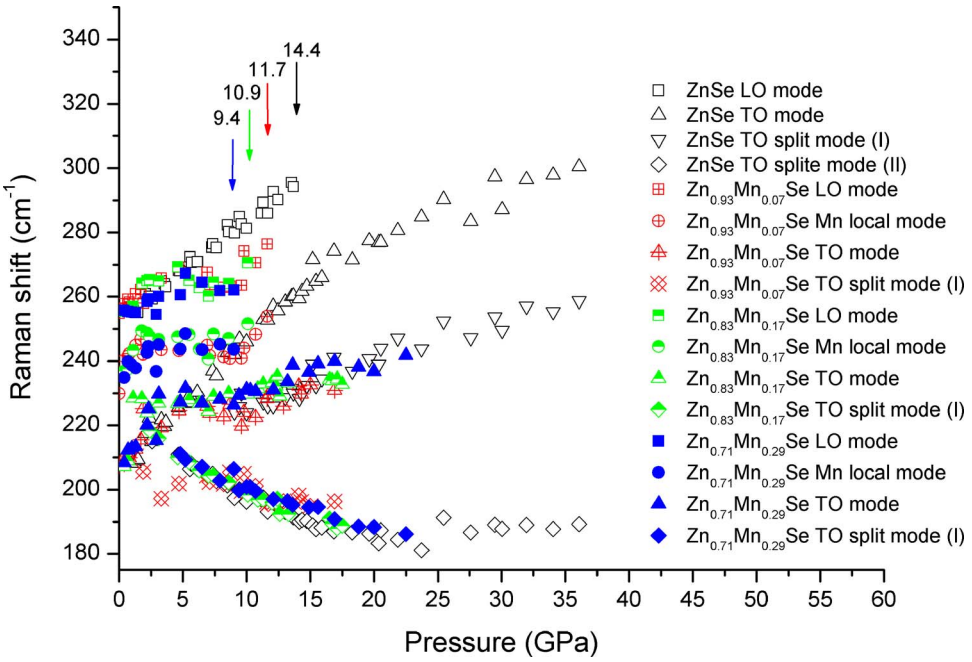

FIG. 4. (Color online) Pressure dependence of Raman peaks in the substrate-free $Zn_{0.71}Mn_{0.29}Se$ (solid symbols), $Zn_{0.83}Mn_{0.17}Se$ (half solid symbols), $Zn_{0.93}Mn_{0.07}Se$ thin films (opened with cross symbols), and ZnSe powder (opened symbols). The arrows at 9.4±0.4, 10.9±0.6, 11.7±0.2, and 14.4±0.3 represent the semiconductor-metal phase transition pressure of substrate-free $Zn_{0.71}Mn_{0.29}Se$, $Zn_{0.83}Mn_{0.17}Se$, $Zn_{0.93}Mn_{0.07}Se$ thin films, and ZnSe, respectively.

polarizability constant (α) is charge×length/(charge/length^2)=length^3. The unit turns out to be one of volume. A thickness around 0.7 μm of our samples and the DAC condition can create the reducing of the Raman spectroscopic quality.

The variations of mode energies as a function of the applying pressure are shown in Fig. 4. In Fig. 4, the pressure dependence of Raman peak positions for substrate-free $Zn_{0.71}Mn_{0.29}Se$ (solid symbols), $Zn_{0.83}Mn_{0.17}Se$ (half solid symbols), $Zn_{0.93}Mn_{0.07}Se$ thin films (opened with cross symbols), and ZnSe powder (opened symbols) is shown. The arrows at 9.4±0.4, 10.9±0.6, 11.7±0.2, and 14.4±0.3 GPa represent the semiconductor-metal phase transition pressures for substrate-free $Zn_{0.71}Mn_{0.29}Se$, $Zn_{0.83}Mn_{0.17}Se$,[6] $Zn_{0.93}Mn_{0.07}Se$ thin films, and ZnSe bulk,[13] respectively. The relationships of the mode frequencies versus pressure for substrate-free $Zn_{0.71}Mn_{0.29}Se$, $Zn_{0.83}Mn_{0.17}Se$, $Zn_{0.93}Mn_{0.07}Se$ thin films were obtained by the quadratic polynomial fitting using the equations as listed in Table II, where ω_i is the wave number in cm^{-1} and p is the pressure in GPa. The effects of pressure on the frequencies of various Raman vibrational modes ω_i, pressure gradient of ω_i, and Grüneisen parameter ν_i of substrate-free $Zn_{0.71}Mn_{0.29}Se$, $Zn_{0.83}Mn_{0.17}Se$, $Zn_{0.93}Mn_{0.07}Se$ thin films at ambient temperature (298 K) are listed in Table III. The Grüneisen parameter (ν_i) for a quasiharmonic mode i of frequency ω_i was defined by Cardona *et al.*[9] The ratio γ_{TO}/γ_{LO}, which relates to the property of ionicity, for substrate-free $Zn_{0.71}Mn_{0.29}Se$, $Zn_{0.83}Mn_{0.17}Se$, and $Zn_{0.93}Mn_{0.07}Se$ thin films is 0.986, 1.143, and 2.543, respectively. This manifests that substrate-free $Zn_{0.93}Mn_{0.07}Se$ thin film has highest ionicity. Our result agrees with that obtained by the previous work in the investigation of bulk crystal.[14] Lin *et al.*[13] reported that the more the ionicity is, the more percentage of the reduction of the semiconductor to metal transition pressure for ZnSe DMS doped with dilute Fe occurs. However, our result on substrate-free $Zn_{1-x}Mn_xSe$ thin films shows that the more the ionicity is, the less percentage of the reduction of the semiconductor to metal transition pressure happens. Therefore, the relationship of ionicity versus the pressure reduction in the semiconductor to metal phase transition for substrate-free $Zn_{1-x}Mn_xSe$ thin films is different from that of ZnSe DMS doped with dilute Fe.

To explain the reason of the reduction of the phase transition pressure of the impurity mixing substrate-free $Zn_{1-x}Mn_xSe$ semiconductor thin films, let us consider the Grüneison parameter of the LO mode in Table III. The Grüneison parameter, γ, is a convenient dimensionless parameter for detecting the effects of anharmonicity.[15] The Grüneison parameter of the LO mode for substrate-free $Zn_{0.71}Mn_{0.29}Se$, $Zn_{0.83}Mn_{0.17}Se$, and $Zn_{0.93}Mn_{0.07}Se$ thin films is 0.265, 0.546,

TABLE II. The quadratic polynomial fitting equation of substrate-free $Zn_{1-x}Mn_xSe$ thin films.

Sample	Raman Modes	Quadratic polynomial fitting equation $\omega_i(i$=LO, Mn local, TO, TO split)=
$Zn_{0.93}Mn_{0.07}Se$ thin film	LO	$257.9+1.09p+0.009p^2$
	Mn local	$239.8+0.35p+0.026p^2$
	TO	$210.5+2.26p-0.064p^2$
	TO split	$202.4+0.28p-0.047p^2$
$Zn_{0.83}Mn_{0.17}Se$ thin film	LO	$257.4+2.24p-0.142p^2$
	Mn local	$241.1+1.60p-0.104p^2$
	TO	$217.2+2.16p-0.071p^2$
	TO split	$225.2-3.37p+0.074p^2$
$Zn_{0.71}Mn_{0.29}Se$ thin film	LO	$252.9+2.91p-0.204p^2$
	Mn local	$235.5+3.24p-0.262p^2$
	TO	$213.3+2.42p-0.056p^2$
	TO split	$220.7-2.32p+0.035p^2$

TABLE III. Effect of pressure on various Raman vibrational modes of substrate-free $Zn_{0.71}Mn_{0.29}Se$, $Zn_{0.83}Mn_{0.17}Se$, and $Zn_{0.93}Mn_{0.07}Se$ thin films and ZnSe bulk, respectively, at ambient temperature (298 K). The values of mode frequencies ω_i, pressure dependence $d\omega_i/dp$, and mode Grüneisen parameter ν_i were extrapolated at ambient conditions.

Sample	Mode	ω_i (cm^{-1})	$d\omega_i/dp$ (cm^{-1} GPa^{-1})	ν_i $[(K_0/\omega_i)(d\omega_i/dp)]$
$Zn_{0.93}Mn_{0.07}Se$ thin film	LO	257.9	$1.09+0.009p$	0.265
	Mn local	239.8	$0.35+0.026p$	0.092
	TO	210.5	$2.26-0.064p$	0.674
	TO split	202.4	$0.28-0.047p$	0.087
$Zn_{0.83}Mn_{0.17}Se$ thin film	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	225.2	$-3.37+0.074p$	−0.939
$Zn_{0.71}Mn_{0.29}Se$ thin film	LO	252.9	$2.91-0.204p$	0.7223
	Mn local	235.5	$3.24-0.262p$	0.8636
	TO	213.3	$2.42-0.056p$	0.7122
	TO split	220.7	$-2.32+0.035p$	−0.6598

and 0.722, respectively. One can note that the increasing of the percentage of the impurity mixing, x, of substrate-free $Zn_{1-x}Mn_xSe$ thin film relates prominently with the increasing percentage of the effects of anharmonicity of the LO mode for our three thin film samples. We can estimate the magnitude of the order of anharmonicity for our three samples. For nearest-neighbor interactions, the Grüneison parameter for a one-dimensional chain (LO mode), with chain length L and lattice spacing a, is defined as $\gamma_{LO}=-(L/\omega_{LO})(d\omega_{LO}/dL)$. Assume that the interaction potential energy has the form $U(z)=U_0+(1/2)\kappa_{LO}z^2+\lambda_{LO}z^3$, where $z=d-a$, d is the distance between the nearest-neighbors, and the parameters λ_{LO} (anharmonic term) and κ_{LO} (harmonic approximation) are coefficients in a Taylor series for the potential $U(z)$. Here we adopt the anharmonic potential model up to third-order term only because the high-order terms have been proved to be negligible in the present analysis. In a one-dimensional chain the frequency scale of the phonon dispersion curve $\omega(\kappa_{LO})$ is determined by a frequency parameter $\omega_{LO}=\sqrt{\kappa_{LO}/m_{LO}}$, where m_{LO} is the reduce mass of a one-dimensional chain. Our goal is to resolve how this frequency depends on the length of the one-dimensional chain. To induce a small change in the length, from L to L', we can apply an external force ΔF. Then we can calculate the second derivative of the potential energy around the equilibrium position, $\kappa'_{LO}=dU^2/dz^2$ for a quasiharmonic system. If a force (pressure) is applied, the potential energy becomes $U(z)=U_0+(1/2)\kappa_{LO}z^2+\lambda_{LO}z^3+\Delta Fz$. The equilibrium position can be found by setting $dU/dz=0$ which yields $\kappa_{LO}\Delta z+3\lambda_{LO}(\Delta z)^2+\Delta F=0$. For a small force, the second order of the displacement can be neglected and thus the solution is approximated to be $\Delta z=-\Delta F/\kappa_{LO}$. The lattice spacing is $a'=a+\Delta z$; the change in the length of the system is $\Delta L=N\Delta z$. The second derivative of the potential energy around the equilibrium position ($\kappa'_{LO}=dU^2/dz^2$ for the quasiharmonic system) is given by $\kappa'_{LO}=\kappa_{LO}+6\lambda_{LO}\Delta z$ and the frequency is

$$\omega'_{LO}=\sqrt{\frac{k'_{LO}}{m_{LO}}}=\frac{(k_{LO}+6\lambda_{LO}\Delta z)^{1/2}}{\sqrt{m_{LO}}}$$
$$=\frac{\sqrt{k_{LO}}\left(1+\frac{6\lambda_{LO}\Delta z}{k_{LO}}\right)^{1/2}}{\sqrt{m_{LO}}}$$
$$=\frac{\sqrt{k_{LO}}\left(1+\frac{1}{2}\frac{6\lambda_{LO}\Delta z}{k_{LO}}+\cdots\right)}{\sqrt{m_{LO}}}$$
$$=\omega_{LO}+\frac{1}{2}\frac{6\lambda_{LO}}{\sqrt{k_{LO}m_{LO}}}\Delta z\,.$$

Therefore, the Grüneison parameter for a one-dimensional chain can be obtained as

$$\gamma_{LO}=-\frac{L}{\omega_{LO}}\frac{\Delta\omega_{LO}}{\Delta L}$$
$$=-\frac{L}{\omega_{LO}}\frac{(\omega'_{LO}-\omega_{LO})}{\Delta L}$$
$$=-\frac{Na}{\omega_{LO}N\Delta z}\frac{3\lambda_{LO}}{\sqrt{\kappa_{LO}m_{LO}}}\Delta z=-\frac{3\lambda_{LO}a}{\kappa_{LO}}.$$

In dimensionless units, for nonsingular functions, these coefficients γ_{LO} are of the order of unity. For the case of interaction potentials assumed in our samples, one finds $\lambda_{LO}<0$ and $\gamma_{LO}>0$ similar to the Lennard–Jones potential of the interaction of two atoms. Therefore, the increasing of the percentage of the impurity mixing, x, of substrate-free $Zn_{1-x}Mn_xSe$ thin films relates the increasing percentage of the effects of anharmonicity and Grüneison parameter of the LO mode. Our observation shows that decreasing in the phase transition pressure P_t for the phase transition from semiconductor to metal phase can be related to the increasing of the percentage of the impurity mixing, x, of substrate-free $Zn_{1-x}Mn_xSe$ thin films by the expression $P_t=[14.1377-29.7673x+47.7178x^2]$ in GPa. Hence, one can conclude that the percentage of the increasing of the Grüneison parameter of the LO mode for semiconductor to metal phase transition might be the important factor for the reduction of phase transition from semiconductor to metal for substrate-free $Zn_{1-x}Mn_xSe$ thin film systems.

IV. CONCLUSIONS

We have carried out high-pressure micro-Raman scattering experiment on substrate-free $Zn_{1-x}Mn_xSe$ thin films, $x=0.07$, 0.17, 0.29, up to around 20.0 GPa at ambient temperature. The existence of the Grüneison parameter of the LO mode causes a reduction in the semiconductor-metal phase transition pressure that is very different from the behavior of bulk crystals. The disappearance of the LO and Mn local phonons is attributed to the metallization of the substrate-free $Zn_{1-x}Mn_xSe$ thin films as same as the behavior of bulk. One component of the visible TO phonon splitting modes in substrate-free $Zn_{1-x}Mn_xSe$ thin film systems was observed up to around 20.0 GPa.

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