Raman Investigation on ZnS, ZnSe, ZnTe Thin Films Obtained by CSVS Technique

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In this work, Raman spectra of zinc sulfide, zinc selenide, and zinc telluride thin film semiconductors deposited by the close-spaced vacuum sublimation technique were investigated. All of the films showed longitudinal optical phonon mode replicas. Varying the substrate temperature results in small shifts of the phonon frequencies in ZnSe and ZnTe, but not in ZnS thin films.

Keywords: Zinc sulfide, Zinc selenide, Zinc telluride, Films, Replica, Phonon, Raman spectroscopy.

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1. INTRODUCTION

Among II-VI semiconductors, zinc sulfide (ZnS), zinc selenide (ZnSe), and zinc telluride (ZnTe) have drawn much attention from researchers for their unique properties and potential for applications such as: a basis layer in light-emitting diodes, photodetectors, gas sensors, X-ray detectors, window (owing to its wide band gap: ZnS-3.7 eV; ZnSe-2.7 eV; ZnTe-2.3 eV) and absorption layers in solar cells, *etc*. [1, 2].

To obtain II-VI semiconductor films, researchers use various methods such as: electro-deposition [3], high-frequency cathode deposition [4], laser impulse and thermal sublimation, hot-wall epitaxy [5], and close-spaced vacuum sublimation (CSVS) [6, 7]. The last method, owing to its unique physical and technological features of evaporator, has a possibility of obtaining high-quality stoichiometric films.

Raman spectroscopy is a powerful tool to investigate the characteristics of semiconductors. However, not many studies have been done to compare zinc blende materials under various depositing conditions. In the present work, Raman spectroscopic investigation of ZnS, ZnSe, and ZnTe films which were deposited at various substrate temperatures was carried out.

2. EXPERIMENTAL DETAILS

Chalcogenide films were obtained by the CSVS technique on well-cleaned glass substrates from stoichiometric powder in VUP-5M vacuum equipment using the following conditions: constant evaporator temperatures were T_{evp} = 1273 K (ZnS); 1073 K (ZnSe), 973 K (ZnTe); the substrate temperature was varied in the range of T_{sub} = (373-673) K for ZnSe and T_{sub} = (423-823) K for ZnS and ZnTe; and the time of evaporation t = 10 min. The detailed description of the deposition device is presented in [8].

Raman spectroscopic measurements were performed at room temperature (297 K) with a TRIAX 550 (1800 grooves/mm) spectrometer, using as excitation sources a He-Cd laser with wavelengths of 325 nm (for ZnS films) and 441.6 nm(for ZnSe films) and an Ar+ laser with a wavelength of 514.5 nm (for ZnTe films). The dispersed signal was detected with a liquid-nitrogen-cooled charge-coupled-device (CCD) detector array. Each spectrum was accumulated 20 times with an acquisition time of 5 sec. each. Long-pass Raman edge filters were used to eliminate Rayleigh scattered light from the laser.

3. RESULTS AND DISCUSSION

Figure 1 (a) shows the Raman spectra of ZnSe thin films grown at various substrate temperatures. All of
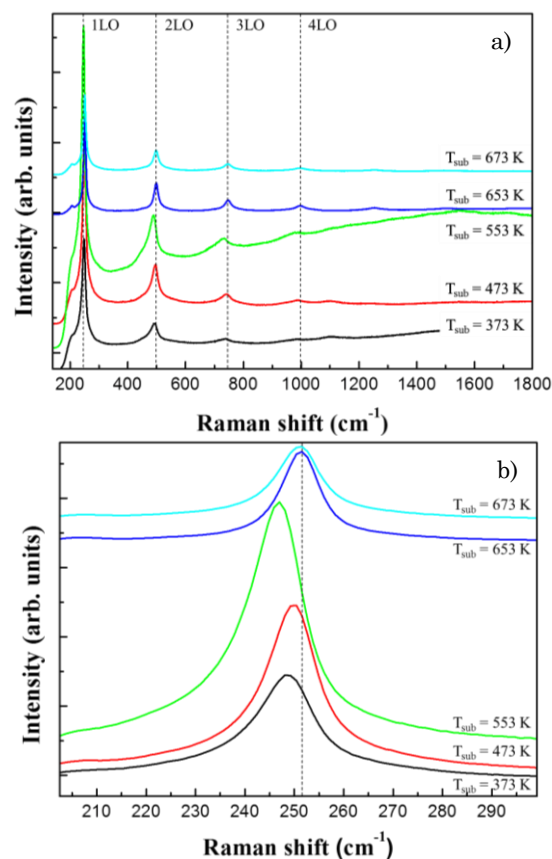

Fig. 1 – Raman spectra of ZnSe films (a) and a detailed view of the 1LO peak (b) for samples grown at indicated substrate temperatures. The dotted line indicates the 1LO frequency for single-crystal ZnSe
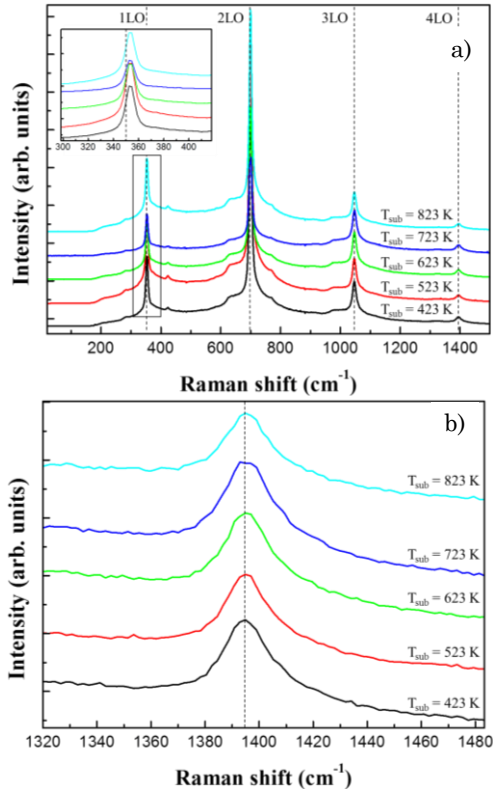
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Fig. 2 – Raman spectra of ZnS films (a) and a detailed view of the 4LO peak (b) for samples grown at indicated substrate temperatures. The inset of (a) shows the 1LO peak, with the dotted line indicating the 1LO frequency for single-crystal ZnS
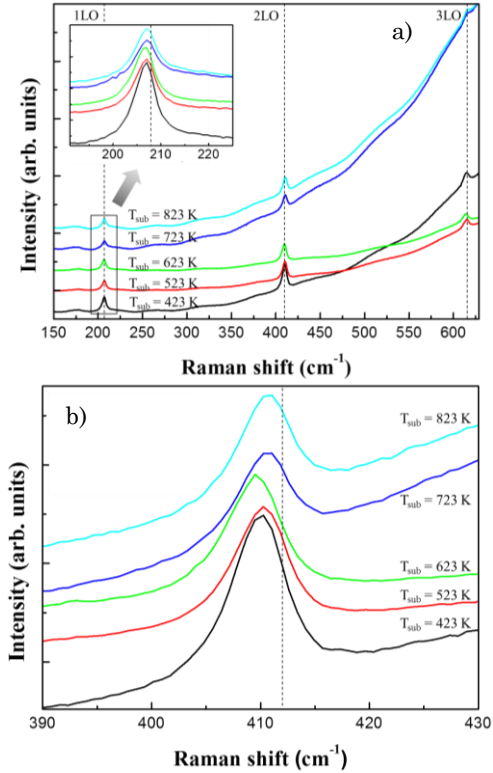

Fig. 3 – Raman spectra of ZnTe films (a) and the inset shows the 1LO peak (b), with the dotted line indicating the 1LO frequency for single-crystal ZnTe. A detailed view of the 2LO peak for samples grown at indicated substrate temperatures. The dotted line indicates the 2LO frequency for single-crystal ZnTe

the samples show the LO mode of ZnSe at around 250 cm^{-1}, which is close to the known frequency for a crystal [9-10] at 252 cm^{-1}.

Also, LO mode replicas are shown for at least up to the fourth order. The LO mode is redshifted relative to the single-crystal ZnSe case. As the temperature of the glass substrate changes, it shifts appreciably as shown in Fig. 1 (b). When the substrate temperature was 373 K, the 1LO appears at 249 cm^{-1}, and it shifts to 250, 247, 251, and 251 cm^{-1} at substrate temperatures of 473, 523, 623, and 673 K, respectively (Table 1). This shift is attributed to the change in the lattice constant caused by induced strain from the substrate. The mismatch in the thermal expansion coefficient of the substrate and the ZnSe thin films would create biaxial strain in the thin film. The redshift indicates a tensile strain. Up to 553 K, the shift gets larger with increased substrate temperature, which indicates that the induced strain also gets larger. For substrate temperatures higher than 653 K, the peak coincides with the 1LO of single-crystal ZnSe, which indicates that the strain is relaxed for these films.

Figure 2 (a) shows the Raman spectra of ZnS thin films deposited at various substrate temperatures. All of the samples show the 1LO mode of ZnS at 352 cm^{-1} and its replicas, which is close to the known frequency for single-crystal ZnS [10]. The 1LO mode is blueshifted relative to the single-crystal case [inset of Fig. 2(a)], which indicates compressive strain. Unlike ZnSe thin films, the peaks do not shift as the T_{sub} changes (Table 1). The higher order do not show any shift, either [Fig. 2(b)]. We can conclude that the overall compressive strain in ZnS is not strongly dependent on the substrate temperature.

Figure 3 (a) shows the Raman spectra of ZnTe thin films deposited at various substrate temperatures. All of the samples show the LO mode of ZnTe at around 207 cm^{-1} which is close to that of a ZnTe crystal at 208 cm^{-1} [11]. The 1LO peak for all the samples seem to coincide within experimental uncertainties. However, the higher order 2LO and 3LO modes show small but definitive shifts with the substrate temperature [Fig. 3(b)]. The trend of peak position shift is somewhat similar to the ZnSe case. The peak redshifts up to T_{sub} = 623 K and then blueshifts toward the bulk peak position as the substrate temperature gets higher (Table 1). Since the redshift is smaller than the case of ZnSe, the strain relaxation occurs at a higher substrate temperature. Furthermore, the 2LO peak frequency for the sample grown at T_{sub} = 823 K does not coincide with that of single crystal ZnTe unlike the case of ZnSe. This indicates that the strain is not fully relaxed. This is also consistent with the smaller redshift.

Judging from the amount of the peak shift, we may conclude that the built-in strain is largest for ZnSe and smallest for ZnS.

4. CONCLUSIONS

We have investigated ZnS, ZnSe, and ZnTe thin films deposited by close-spaced vacuum sublimation technique by Raman spectroscopy. All of the samples show their LO modes and the replicas which demonstrate their high quality. Their shifts are interpreted as

being due to the built-in strain caused by thermal expansion mismatch between the substrate and the film. ZnSe and ZnTe thin films grown at higher substrate temperatures exhibit strain relaxation. We can conclude that the built-in strain is largest for ZnSe and smallest for ZnS.

Table 1 – List of Raman peak frequencies in investigated films

ZnSe										
T_{sub}	373 K		473 K		553 K		653 K		673 K	
ν	cm^{-1}	eV	cm^{-1}	eV	cm^{-1}	eV	cm^{-1}	eV	cm^{-1}	eV
1LO	250	0.0310	249	0.0309	248	0.0308	249	0.0309	251	0.0309
2LO	494	0.0613	497	0.0616	491	0.0609	501	0.0621	500	0.0621
3LO	743	0.0921	746	0.0925	735	0.0911	749	0.0929	749	0.0929
4LO	995	0.1230	995	0.1230	984	0.1220	998	0.1240	998	0.1240
ZnS										
T_{sub}	423 K		523 K		623 K		723 K		823 K	
ν	cm^{-1}	eV	cm^{-1}	eV	cm^{-1}	eV	cm^{-1}	eV	cm^{-1}	eV
1LO	352	0.0436	352	0.0436	352	0.0436	352	0.0436	352	0.0436
2LO	699	0.0867	699	0.0867	699	0.0867	699	0.0867	699	0.0867
3LO	1046	0.1300	1046	0.1300	1046	0.1300	1046	0.1300	1046	0.1300
4LO	1395	0.1730	1395	0.1730	1395	0.1730	1395	0.1730	1395	0.1730
ZnTe										
T_{sub}	T_s = 423 K		T_s = 523 K		T_s = 623 K		T_s = 723 K		T_s = 823 K	
ν	cm^{-1}	eV	cm^{-1}	eV	cm^{-1}	eV	cm^{-1}	eV	cm^{-1}	eV
1LO	207	0.0257	207	0.0257	203	0.0255	207	0.0257	207	0.0257
2LO	410	0.0508	410	0.0508	409	0.0507	411	0.0510	411	0.0510
3LO	615	0.0763	615	0.0763	614	0.0761	616	0.0764	616	0.0764
4LO	821	0.1020	821	0.1020	819	0.1020	-	-	-	-

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