Raman study of phonon modes and disorder effects in Pb$_{1-x}$Sr$_x$Se alloys grown by molecular beam epitaxy

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We report phonon modes and alloy disorder effects of Pb$_{1-x}$Sr$_x$Se alloys ($x \leq 0.3$) grown on BaF$_2$ (111) substrates by Raman spectroscopy measurements. On the basis of phonon modes in binary PbSe and SrSe, first-, second-, and high-order Raman scattering phonon frequencies of ternary Pb$_{1-x}$Sr$_x$Se are observed, together with the deduction of the disorder activated modes due to the breakdown of the selection rule. The alloy disorder is found to play a more important role than the strain effect in Pb$_{1-x}$Sr$_x$Se, and has been further investigated by employing the special correlation model. The PbSe-like second-order features are also shown to broaden slightly and diminish in intensity with increasing Sr concentration, which has been attributed to a weak breakdown in the long-range order. © 2006 American Institute of Physics. [DOI: 10.1063/1.2159079]

I. INTRODUCTION

Considerable interest is being devoted recently to the lead salt IV-VI PbSe-based materials because of their unique optoelectronic and structural properties. Good quality PbSe-based thin films with excellent homogeneity can be epitaxially grown on low-cost BaF$_2$ (Refs. 1 and 2) and silicon$^3$ substrates. Alloysing Sr can widely tune the energy band gap (0.28–3.40 eV) within the ternary Pb$_{1-x}$Sr$_x$Se system. The absence of a heavy hole band in Pb$_{1-x}$Sr$_x$Se thin films reduces the nonradiative Auger recombination rate by one or two orders of magnitude lower than that of narrow band gap III-V and II-VI materials.$^2$ This allows the appearance of stimulated emission at relatively low generation rates. Near room-temperature emission has been demonstrated in both PbSrSe/PbSe double heterostructure lasers$^4$ and vertical-cavity surface-emitter lasers$^5$ in the wavelength range from 3.0 to 5.1 μm. We have reported strong room-temperature infrared detection in Pb$_{1-x}$Sr$_x$Se within 1.0–3.1 μm,$^7$ in addition to a detailed temperature-dependent absorption and photoluminescence investigation of Pb$_{1-x}$Sr$_x$Se thin films and PbSrSe/PbSe quantum well structures for midinfrared laser applications.$^8,9$ PbSr(Se,Te) with low dimensional structures are also found to be interesting candidate materials for thermoelectric applications.$^10$

Despite the technological importance of the IV-VI alloy semiconductors, many microscopic vibrational properties of these systems are not well understood yet. In fact, knowledge of lattice vibrations in semiconductors will establish an important base in the fields of optoelectronics, heat transport, and quantum electronics. However, only a few studies of phonon modes for Pb$_{1-x}$Sr$_x$Se alloy have been reported, including its two end members. Although Raman and reflection results have been published preliminarily by Yang et al.$^{11}$ Kaneko et al.$^{12}$ and Jiang et al.$^{13}$ for the two binary PbSe and SrSe, respectively, the phonon information from their analysis is still incomprehensive. In our previous work,$^{14}$ we had employed the far-infrared reflection measurement to obtain the long-wavelength optical phonons and revealed mixed mode behavior in Pb$_{1-x}$Sr$_x$Se using the modified random-element-isodisplacement model. However, the frequencies of the transverse-optical (TO) phonons of Pb$_{1-x}$Sr$_x$Se were calculated through fitting and the longitudinal-optical (LO) phonons were estimated from the Kramers-Kronig calculation. More direct and accurate work upon phonon behavior in Pb$_{1-x}$Sr$_x$Se is required. In addition to the phonon modes in Pb$_{1-x}$Sr$_x$Se alloy, the potential fluctuations related to the alloy induced disorder on a microscopic scale are also one of the characteristic aspects of substitutional ternary semiconductors. In particular, alloy disorder in most of the mixed crystals plays a major role in the crystal quality issue, which needs more attention to be paid for.

Raman scattering not only is the most direct and nondestructive way to study the phonons of materials, but also can yield important information about structural order in the lattice on a scale of a few lattice constants. In this article, we investigate the Raman scattering of ternary Pb$_{1-x}$Sr$_x$Se thin films for the complete phonon characteristics. The first-, second-, and high-order phonon scattering of Pb$_{1-x}$Sr$_x$Se ($x = 0.3$) have been clearly assigned. In addition to the identification of the disorder activated modes caused by the breakdown of the selection rule, we have explicated the alloy induced disorder effects in ternary Pb$_{1-x}$Sr$_x$Se alloys by the aid of the special correlation model (SCM).

II. EXPERIMENTAL DETAILS

Five Pb$_{1-x}$Sr$_x$Se thin film samples were grown on freshly cleaved BaF$_2$ (111) substrates by molecular-beam epitaxy (MBE) techniques in an Intevac GEN II Modular system. PbSe, Se, and Sr were used as source materials. The Sr content $x$ in the five samples is 0 (PbSe), 0.066, 0.171, 0.276, and 1.0 (SrSe), respectively, which have been confirmed by x-ray diffraction, absorption and photoluminescence.
The quite easy oxidation of the thin film with a step scan resolution of 0.6 signal distinguishing ability in the direction perpendicular to the aid of the confocal setup, this Raman system has a high temperature with a high resolution better than 0.5 cm\(^{-1}\). By LabRAM HR 800 UV micro-Raman spectrometer at room scattering measurements were carried out on a Jobin Yvon approximately 88 and 143 cm\(^{-1}\). It is well known that PbSe scattering configuration. The observed dominant peaks are power less than 10 mW, and the acquisition time was 20 s. As a result, Raman scattering of forbidden LO modes in the Raman peaks to the phonon modes, we reference the theoretical PDC is out of our experimental range due to the theoretically calculated phonon dispersion curve of PbSe.

III. RESULTS AND DISCUSSION

Figure 1 shows the Raman spectrum of the PbSe thin film ranging from 50 to 600 cm\(^{-1}\) taken in the \(z(x, -)z\) backscattering configuration. The observed dominant peaks are approximately 88 and 143 cm\(^{-1}\). It is well known that PbSe possesses the rock-salt structure, and its first-order Raman scattering is symmetry forbidden due to the central inversion. However, calculation shows that both LO and TO phonons in PbSe on the (111) oriented surface are not strictly Raman inactive in the backscattering geometry,\(^{11}\) and slight violation of the translational symmetry may also activate such scattering. As a result, Raman scattering of forbidden LO modes in lead chalcogenides have been observed.\(^{15,16}\) To assign the Raman peaks to the phonon modes, we reference the theoretically calculated phonon dispersion curve (PDC) of PbSe (shown in the inset of Fig. 1) by considering the effects of van der Waals interactions, free-carrier doping, and three-body interactions in the framework of both-ions (anions and cations) polarizable rigid shell model.\(^{17}\) From the frequency point of view, it is straightforward that the observed Raman peaks around 143 cm\(^{-1}\) corresponds well to the first-order LO mode of PbSe. The TO phonon of \(\sim 47\) cm\(^{-1}\) in the theoretical PDC is out of our experimental range due to the limitation of our Raman scattering system. Nevertheless, the second-order TO (2TO) phonon scattering at 88.4 cm\(^{-1}\) can be clearly observed in our spectrum, indicating that the TO mode phonon frequency is about 44.2 cm\(^{-1}\) for PbSe. This kind of frequency discrepancy is understandable, since the theoretical PDC is based on the bulk material, whereas our sample is thin film.

Besides the first-order phonon modes, the Raman spectrum in Fig. 1 also reveals the second- and high-order phonon scattering. According to the PDC, we can assign most of the Raman structures, and have marked the origin of all of the Raman peaks in Fig. 1, though the assignment for high-order modes may not be unique. In addition, we note that the feature at 243 cm\(^{-1}\) is very close to the LO frequency of the BaF\(_2\) substrate, but we can easily rule out that possibility, since (i) the energy of incident photons (2.41 eV) is much higher than the band gap of PbSe (0.28 eV), and the light is absorbed entirely by the 1-\(\mu\)m-thick PbSe thin film, detection of the signal from the BaF\(_2\) substrate is highly improbable; (ii) the intensity of this feature is observed to be weaker and weaker when the incident light is focused gradually from the PbSe film to the BaF\(_2\) substrate (same as the schematic shown in the inset of Fig. 2); and (iii) this peak is found to redshift with the increase of Sr content in Pb\(_{1-x}\)Sr\(_x\)Se alloys. We can therefore attribute it to the two-phonon scattering process 2LO(\(\Delta\)) from PbSe, which is in agreement with the value of 244 cm\(^{-1}\) in the PDC.

Figure 2 displays the Raman spectra of SrSe at different light focus depths along the layer from the thin film to the substrate. The peak at 145 cm\(^{-1}\) is from the TO phonon scattering of SrSe, which is close to the reported TO of 141 cm\(^{-1}\).
The clear understanding of the phonon modes in binary SrSe and PbSe establishes the base for proper analysis of the phonons and disorder effects in Sr incorporated Pb$_{1-x}$Sr$_x$Se thin films. Figure 3 shows the Raman spectra of ternary Pb$_{1-x}$Sr$_x$Se with the dominant PbSe-like LO mode at 143 cm$^{-1}$. The peaks at 87, 241, and 284 cm$^{-1}$ in the spectra are the second-order PbSe-like modes, whereas the features in the range from 350 to 600 cm$^{-1}$ are high-order scattering in Pb$_{1-x}$Sr$_x$Se alloys. We have summarized all the observed first-, second-, and high-order phonon frequencies from Raman spectroscopy of the alloys in Table I, where the phonon information of PbSe and SrSe are also included. It is understandable that most of the phonon scattering in ternary Pb$_{1-x}$Sr$_x$Se only has the PbSe-like characteristics due to the low concentration of Sr in ternary PbSrSe, where two-mode behavior has been observed for the studied concentration. Actually the observed SrSe-like LO mode in the high Sr content sample ($x=0.276$) and pure SrSe is very weak. Moreover, in comparison with the results in Ref. 14, we find that we have obtained higher frequencies for the SrSe-like LO modes in both Pb$_{0.72}$Sr$_{0.28}$Se and pure SrSe by Raman scattering. We think that the discrepancy arises from the different experimental methodologies. In Ref. 14, we have first employed the far-infrared reflection spectra to yield the energies of TO phonons, and then estimated the LO phonon frequencies from the Kramers-Kronig calculation. Here, we use the straightforward Raman scattering to directly reveal the accurate results.

Besides the well assigned PbSe- and SrSe-like modes, we find two additional Raman features near 97 and 114 cm$^{-1}$ in the alloys, which have comparable intensity to the dominant PbSe-like LO modes particularly in the Pb$_{0.934}$Sr$_{0.066}$Se sample. Generally, we should attribute them to the SrSe-like phonon modes because Pb$_{1-x}$Sr$_x$Se has two modes in that composition region. However, this kind of assignment is not suitable for these two Raman features (97 and 114 cm$^{-1}$) because of the following arguments and experimental facts: (i) the intensity of these two features decreases with the increasing Sr concentration; (ii) their frequencies redshift as Sr increases, in contrast to the expected blueshift of the SrSe-like phonon modes; and (iii) in a Pb-rich sample of Pb$_{1-x}$Sr$_x$Se, a PbSe-like mode is expected to propagate, while a SrSe-like mode would be more like a gap mode with an amplitude of vibration decaying away from the impurity atom.

As we know, the alloying induced disorder will lead to

![FIG. 3. The Raman spectra of Pb$_{1-x}$Sr$_x$Se alloys ($x=0.066$, 0.171, and 0.276) from 50 to 600 cm$^{-1}$.](image-url)
of Sr atoms, we cannot detect these modes in the Raman
the DALA and DATO modes in the Pb-rich composition re-
fore, we can attribute these two structures correspondingly to
are quite close to those of the observed new modes. There-
PbSe-like LO phonons on Sr concentration in Pb\textsubscript{1−x}Sr\textsubscript{x}Se alloys. The solid
in curves (b) and (d) are the fitting results, whereas the dashed curve in (c)
is guide to eyes.

the breakdown of the translational symmetry in mixed crys-
tals and further bring new vibration modes. In this case, the
phonons at Brillouin zone edges, where the phonon density of
states are generally high, will also contribute to the first-
order Raman scattering, which are usually referred as disor-
der activated (DA) modes. According to the PDC of PbSe, the frequencies of zone-edge longitudinal-acoustical (LA)
and TO phonons are 99 and 113 cm\textsuperscript{-1}, respectively, which
are quite close to those of the observed new modes. There-
fore, we can attribute these two structures correspondingly to
the DALA and DATO modes in the Pb-rich composition re-
ion. As such modes will only be activated by the presence of
Sr atoms, we cannot detect these modes in the Raman
scattering of pure PbSe, and the observation of these kinds of
modes is taken as the evidence of disorder in the alloy.

Figure 4(a) plots the enlarged Raman feature of PbSe-
like LO mode in Pb\textsubscript{1−x}Sr\textsubscript{x}Se. The frequency of the mode
displays redshift with Sr concentration, and the full width at
half maximum (FWHM) basically increases with x, as shown in
Figs. 4(b) and 4(c). Further, Raman line shape of this mode
displays a small asymmetric Lorentzian profile in Pb\textsubscript{1−x}Sr\textsubscript{x}Se alloys, in contrast to the widely observed strong
asymmetric Raman shape in some alloys such as Cd\textsubscript{1−x}Se\textsubscript{x}
and In\textsubscript{1−x}Ga\textsubscript{x}As.\textsuperscript{19} This is because the strong asymmetry
mainly arises from contribution of the DA mode at the low
energy side, whereas the DA modes in our Pb\textsubscript{1−x}Sr\textsubscript{x}Se are not
overlapped by the LO mode.

It has been reported that the FWHM and the profile of
Raman spectra will depend on both the strain from the lattice
mismatch and alloy disorder of the thin film. In a mis-
matched heteroepitaxial system, the accommodation of the
lattice mismatch will produce the strain if the epitaxial layer
is thinner than a critical value $t_c$; whereas for the thickness
larger than $t_c$, the strain will be released. The lattice constant
of BaF\textsubscript{2} substrate is 6.202 Å, while the constant
d(Pb\textsubscript{1−x}Sr\textsubscript{x}Se) of the thin film can be derived from the Veg-
ard’s law by linear interpolation between the value of
d(PbSe)=6.124 Å and d(SrSe)=6.225 Å,\textsuperscript{20} which yields
d(Pb\textsubscript{1−x}Sr\textsubscript{x}Se)=6.124+0.101x (Å). According to the energy
balance model,\textsuperscript{21} we can calculate the critical thickness $t_c$
to be 0.1 μm for Pb\textsubscript{1−x}Sr\textsubscript{x}Se layer on BaF\textsubscript{2} substrate, which is
much thinner than the sample thickness of ~1 μm. As a result,
the effect of strain on the Raman profile of PbSrSe is trivial. The weak strain effect in PbSrSe/BaF\textsubscript{2} material also
exhibits itself in the frequency shift, which can be expressed
on the dependency of Sr concentration by least square fitting
as: $\omega^{\text{PbSe-like}}(x)=143.4−9.89x$ [the solid line in Fig. 4(b)].
We find that the frequency shift in Pb\textsubscript{1−x}Sr\textsubscript{x}Se is much smaller
than that of the strain dominant alloys.\textsuperscript{22} In addition to the
strain, the compositional fluctuation will also induce fre-
quency shift of some Raman-active modes in alloys.\textsuperscript{23}

We now employ the well known SCM to analyze the
disorder effects. The model is based upon the relaxation of
the $q=0$ selection rule, induced by the microscopic nature of
disorder in the alloys which yields a finite phonon mode
dependence. The scattering intensity is described by the fol-
lowing formula:\textsuperscript{24}

\begin{equation}
I(\omega) \propto \int_{0}^{1} \exp(-q^2L^2/4) d^3q [\omega - \omega(q)]^2 + (1/2)^2,\end{equation}

where $q$ is the wave vector in the unit of $2\pi/d$, $d$ is the
lattice constant of Pb\textsubscript{1−x}Sr\textsubscript{x}Se, $L$ is the correlation length (Å),
and $\Gamma$ is the linewidth of the PbSe-like LO phonon. For the
dispersion $\omega(q)$ of the LO phonon, results of the one dimen-
sional linear-chain model can be used:\textsuperscript{25}

\begin{equation}\omega(q)^2 = A + B[1 - \cos(q\pi)]^{1/2},\end{equation}

where the constants $A=1/2\omega_0^2(x)$ and $B=(1/2)\omega_0^2(x)m\mu/(m+\mu)^2$ with the Se mass of
m\textsubscript{Se}=78.96 amu and weighted mean mass of $\mu=(1-x)M_{\text{Pb}}+xM_{\text{Se}}$ ($M_{\text{Pb}}$
=207.2 amu and $M_{\text{Se}}=87.62$ amu). $\omega_0(x)$ is the phonon fre-
quency at the zone center. The spatial correlation length $L$
can be assumed as a measure of the extent to which the
lattice is ordered, since the disruption in the periodicity is the
cause of the finite spatial correlation of the phonon wave
function. For simplicity, the integration on the right-hand
side of Eq. (1) is taken in a spherical Brillouin zone.

Figure 4(a) plots the least square fit (dashed curves) of
Eq. (1) to the experimental data (solid curves) of the PbSe-
like LO phonons in Pb\textsubscript{1−x}Sr\textsubscript{x}Se. Figures 4(c) and 4(d) show the fitted parameters $\Gamma$ and $L$ as a function of Sr concen-
tration. With increasing Sr content, $\Gamma$ increases whereas $L$
decreases. The larger $\Gamma$ value implies the shorter phonon relax-
tion time leading from the higher density of defects or
dislocations, which are induced mainly by the alloy disorder
in Pb\textsubscript{1−x}Sr\textsubscript{x}Se. As the PbSe-like phonon modes are consid-
ered to be localized in the PbSe regions, $L$ represents the
average size of the localized region of PbSe-like phonons.
The calculated phonon coherence length $L$ decreases with
increasing Sr concentration, which indicates that the phonon
extended region becomes smaller in higher Sr content as a
result of the alloy disorder. The large disorder in Pb\textsubscript{1−x}Sr\textsubscript{x}Se

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig4.png}
\caption{(a) The PbSe-like LO phonon spectra of Pb\textsubscript{1−x}Sr\textsubscript{x}Se, where the
redshift of the band is observed with increasing x. Dependence of the (b)
phonon frequency (c) linewidth, and (d) spatial correlation length of
the PbSe-like LO phonons on Sr concentration in Pb\textsubscript{1−x}Sr\textsubscript{x}Se alloys. The solid
plots the least square fit curves, whereas the dashed curve in (c)
is guide to eyes.}
\end{figure}
reflected in Raman scattering process is mainly due to the fact that the substitutional element Sr is from a different group (II for Sr versus IV for Pb) with different outer electrons. Furthermore, we also find that the degree of disorder is approximately proportional to the product of Sr and Pb compositions \( x(1-x) \) and the solid curve in Fig. 4(d) is the fitted result of \( L=69-116x(1-x) \) (Å), revealing the maximum disorder when the Sr atoms substitute half of the Pb atoms in PbSe.

The second-order Raman scattering in ternary \( \text{Pb}_{0.934}\text{Sr}_{0.066}\)Se and \( \text{Pb}_{0.829}\text{Sr}_{0.171}\)Se is believed to be PbSe-like according to the phonon frequencies (see Table I). Although in Raman scattering of a relatively high Sr incorporated \( \text{Pb}_{0.725}\text{Sr}_{0.275}\)Se sample, in addition to the PbSe-like phonons, we can identify the second-order SrSe-like phonons at 396 cm\(^{-1}\)(TO+LO) and 513 cm\(^{-1}\)(2LO), together with the first-order SrSe-like LO phonons as mentioned previously. Not only the PbSe-like first-order modes, but also the observed PbSe-like second-order phonons exhibit redshift with increasing Sr content. Figures 1 and 3 have clearly displayed the rapid degradation of the fairly sharp PbSe-like 2TO(\( \Gamma \)), 2LO(\( \Delta \)), and 2LO(\( \Gamma \)) second-order features. For pure PbSe, these Raman structures are narrow and well observed above the underlying two-phonon continuum. However, in ternary \( \text{Pb}_{1-x}\text{Sr}_{x}\)Se, these features decrease in relative strength and broaden slightly. Since second-order Raman process is a sensitive test of crystalline quality, we interpret these results as the evidence of weakly diminishing long-range order with increasing Sr concentration, which is in good agreement with our previous discussion.

**IV. CONCLUSIONS**

In summary, we have reported the characteristics of the first-, second-, and high-order scattering in \( \text{Pb}_{1-x}\text{Sr}_{x}\)Se (for \( x \leq 0.3 \)) and PbSe, as well as the TO and LO phonons in SrSe by Raman scattering measurements. The disorder induced DATO and DALA modes in ternary \( \text{Pb}_{1-x}\text{Sr}_{x}\)Se have been observed. The alloying disorder plays a key role in \( \text{Pb}_{1-x}\text{Sr}_{x}\)Se alloy in the Raman scattering process and the calculated phonon coherence length \( L \) in SCM demonstrates that the disorder increases with Sr concentration, which also can be confirmed by the second-order PbSe-like structures in \( \text{Pb}_{1-x}\text{Sr}_{x}\)Se.

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