Journal of Alloys and Compounds 478 (2009) 41–44

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Plasmon–phonon interaction in $Hg_{1-x}Mn_xSe$ alloys

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ARTICLE INFO

Article history:
Received 8 October 2008
Received in revised form
21 November 2008
Accepted 26 November 2008
Available online 7 December 2008

Keywords:
Semiconductors
Infrared spectroscopy
Optical properties
Light absorption and reflection

ABSTRACT

Far-infrared reflection and Raman spectra of $Hg_{1-x}Mn_xSe$ ($x \leq 0.3$) alloys were measured at room temperature. The analysis of the Raman spectra was made by deconvolution technique. The analysis of the far-infrared spectra was made by a fitting procedure based on dielectric function which includes spacious distribution of free carrier influence on the plasmon–phonon interaction. In spite of strong plasmon–LO phonon interaction, we found that the long wavelength optical phonon modes of these mixed crystals showed two-mode behaviour. The model of phonon behaviour was developed, and we obtain very good agreement with experimental results.

1. Introduction

$Hg_{1-x}Mn_xSe$ is diluted magnetic semiconductor (DMS) [1] where a fraction of nonmagnetic Hg atoms is randomly replaced by Mn^{2+} ions. DMSs have attracted considerable attention due to many interesting properties like: different magnetic phases (spin glass, paramagnetic or antiferromagnetic); possibility of purposely changing of the zone structure parameters and the lattice constants by varying of composition; huge negative magnetoresistance.

$Hg_{1-x}Mn_xSe$ crystallizes in the zinc-blende structure, as its parent HgSe, in the entire range of solubility of MnSe in HgSe, $0 < x < 0.38$ [2]. At room temperature, the HgSe energy gap is −30 meV [3]. For low values of x, $Hg_{1-x}Mn_xSe$ is a zero-gap semiconductor like HgSe. At several atomic percent of Mn ($x = 0.065$ at 4.2 K) energy gap opens and for larger values of x $Hg_{1-x}Mn_xSe$ becomes an narrow-gap semiconductor, with the energy gap extremely sensitive to x [4].

In the far-infrared spectra of mercury chalcogenide zero-band gap semiconductors HgTe [5] and HgSe [6], beside zone center mode, an additional mode appears at frequencies lower then those of zone-center mode. Also, this additional structure was observed in $Hg_{1-x}Mn_xTe$ [7] and $Hg_{1-x}Mn_xSe$ alloys [4] at the same frequencies as in HgTe [5] and HgSe [6], and was assigned as resonant mode that corresponds to frequency difference of $\omega_{TO} - \omega_{TA}$ at the X-point of Brillouin zone. The temperature dependence of resonant two-phonon mode intensity (decreasing with lowering the temperature like in HgTe [5] and in HgSe [6]) is connected with the variation of phonon and electron distributions. In mixed crystals, this structure should vanish without changing its energy when the energy gap is opened. In $Hg_{1-x}Mn_xSe$ [4], the intensity of this mode slightly decreases with increasing of the temperature, and still exists in the samples with Mn concentration $x > 0.065$ (at $T = 4.2$ K), when $Hg_{1-x}Mn_xSe$ samples are no longer zero- but narrow-band gap semiconductors. The similar is found in $Hg_{1-x}Cd_xTe$ system [8].

Till now optical properties of $Hg_{1-x}Mn_xSe$ were researched in few papers [4,9]. But, the objects of investigation were mixed crystals with a weak plasmon–LO phonon interaction. In our research we investigate the whole range of concentration from zero gap to positive-open gap material where, for the latter case, we have strong plasmon–LO phonon interaction.

2. Sample characterization and experiment

The crystals of $Hg_{1-x}Mn_xSe$ were grown by the Bridgman technique. Samples were prepared by standard procedure. After mechanical treatment, in order to ensure that the surface is free of mechanical damages, samples were etched in 5% bromine solution in methanol. Samples are of n-type, like HgSe, and have concentration of electrons about 10^{17} cm^{-3}.

The concentration of manganese in the $Hg_{1-x}Mn_xSe$ crystals was checked by measuring atomic absorption (ICP-AS PerkinElmer 6500).

X-ray diffraction analysis was performed on a Philips powder diffractometer PW1010 using Cu Kα1, α2 radiation at room temperature.

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doi:10.1016/j.jallcom.2008.11.145

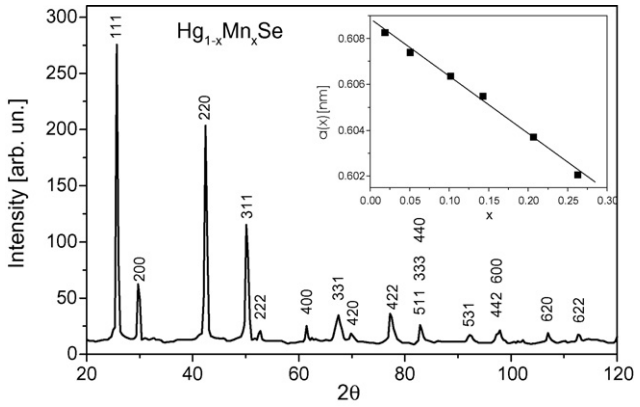

Fig. 1. X-ray diffractogram of powdered $Hg_{0.9}Mn_{0.1}Se$ single crystal. Insert: lattice constant vs. manganese mole fraction for $Hg_{1-x}Mn_xSe$. The Vegard's rule is presented by full line: $a(x) = (0.6087 - 0.024x)$ nm.

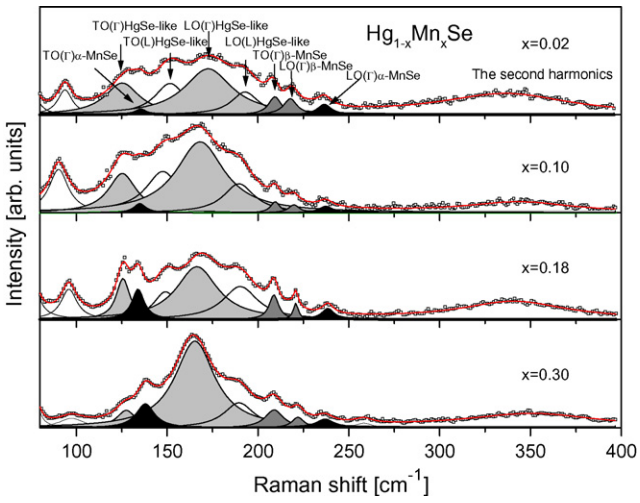

Fig. 2. Raman spectra of $Hg_{1-x}Mn_xSe$ alloys recorded at 300 K in the frequency range from 80 to 400 cm^{-1} for different contents of manganese. The most pronounced peaks represent β-HgSe-like LO and TO modes from the centre of Brillouin zone; noncolored peaks originated from the L-point of Brillouin zone; grey colored Lorentians are β-MnSe-like TO and LO modes and black Lorentians present non-alloyed α-MnSe modes.

Raman measurements were performed in the back scattering geometry by using a Joben–Yvon U1000 spectrometer. Phonon spectra were exited by Ar-ion laser line with $\lambda = 514.5$ nm. Spectra were measured at room temperature.

Far-infrared reflectivity measurements were made in spectral range (50–500 cm^{-1}) at room temperature with BOMEM DA8 spectrometer.

3. Results and discussion

3.1. X-ray measurements

Fig. 1 presents X-ray diffractogram for powdered $Hg_{0.9}Mn_{0.1}Se$ single crystals. The spectra show the zinc-blend cubic structure. The unit cell parameter was determined using both Rietveld analysis and standard procedure. As we see from insert in Fig. 1 the unit cell parameter (a) vs. manganese concentration (x) obeys the Vegard's rule [2].

3.2. Raman scattering measurements

Raman spectra of $Hg_{1-x}Mn_xSe$ alloys recorded at 300 K in the frequency range from 80 to 400 cm^{-1} for different contents of manganese are presented as open squares in Fig. 2. The deconvolution of spectra shows that there exist modes that are not obeyed by selection rules.

On the basis of neutron scattering studies of HgSe and phonon dispersion relations, Fig. 3, [10] we recognized HgSe–like modes in the Raman spectra of $Hg_{1-x}Mn_xSe$. The peak at 94 cm^{-1} corresponds to a local extreme on a phonon density of states of HgSe and becomes Raman active due to disorder-induced relaxation of selection rules. The mode at 126 cm^{-1} is HgSe-like TO mode from the center of Brillouin zone (BZ). The highest intensity mode, at 174 cm^{-1}, may be assigned as a zone center HgSe-like LO Raman active phonon and modes about 150 and 190 cm^{-1} are disorder-activated modes that originate from the L-point of Brillouin zone.

Weak modes at about 135 and 235 cm^{-1} depend to α-MnSe with stabile rock-salt structure and show that some amount of MnSe is not incorporated (alloyed) in $Hg_{1-x}Mn_xSe$ solid solution. The absence of α-MnSe lines in the X-ray diffractogram, Fig. 1, suggests that the amount of α-MnSe is under the limit of error. Remained modes at 209 and about 220 cm^{-1} are β-MnSe-like modes from the center of Brillouin zone. At about 340 cm^{-1} is the maximum of a group of some higher harmonic modes. Some modes observed in the Raman spectra of $Hg_{1-x}Mn_xSe$ are shown in Fig. 5b as a function of Mn-content. Solid black circles present TO and LO modes of HgSe from the center of BZ, solid squares present β-MnSe modes and open triangles are LO and TO modes of HgSe from the L-point of BZ.

3.3. Far-infrared reflectivity measurements

FIR reflection spectra of $Hg_{1-x}Mn_xSe$ ($x = 0.05$, 0.10, 0.14, 0.20, 0.26) recorded in energy range from 50 to 400 cm^{-1} at room temperature are shown in Fig. 4 with experimental data presented by circles. We can see the difference in spectra between samples with $x = 0.05$ and, to some extent $x = 0.10$, where the plasma edge is on the higher frequencies and partially screens the phonons, and samples where the gap is more open, where plasma frequency decreases and leaves very clear phonon modes.

The classical dielectric function [4], based on an independent oscillators model and Drude expression for the free carrier contribution, is insufficient for description of strong plasmon–LO phonon interaction, in $Hg_{1-x}Mn_xSe$ alloys. We use the bonded oscillators model and dielectric function that takes in account the existence of plasmon–phonon coupling [11]. The lines, shown in Fig. 4, are

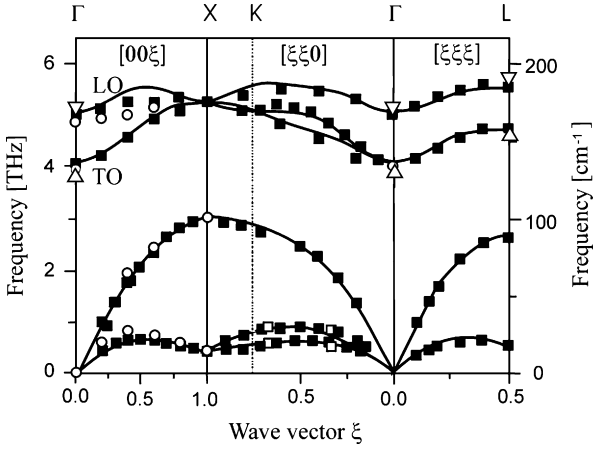

Fig. 3. Phonon dispersion of HgSe. Picture is taken over from Ref. [10]. Added triangles present frequencies obtained by Raman scattering on $Hg_{0.98}Mn_{0.02}Se$.