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OPTICAL CHARACTERIZATION OF MBE-GROWN $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ LAYERS BY RAMAN SPECTROSCOPY*

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In this paper we discuss a possibility of an optical characterization of thin semiconductor epilayers by Raman scattering measurements. As an example zinc blende $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ epilayers ($0.66 \leq x \leq 1.0$) have been grown by molecular beam epitaxy method and investigated by Raman scattering and X-ray diffraction. Information resulting from both methods is compared and discussed.

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1. Introduction

Bulk crystals of semimagnetic semiconductor $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ obtained by equilibrium growth techniques crystallize in the cubic (zinc blende) structure only for $x \leq 0.7$. One can obtain a metastable zinc blende $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ for $0.7 < x \leq 1.0$, e.g., by molecular beam epitaxy (MBE) on substrates of cubic symmetry [1].

2. Growth

Thin films of zinc blende $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ crystals with $0.66 \leq x \leq 1.0$ were grown in the Institute of Physics, Polish Academy of Sciences in Warsaw using EPI 620 MBE system on semi-insulating (001) GaAs wafers. The crystal growth was performed for various ratios of Mn, Te and Cd (or CdTe) fluxes resulting in growth rate of $0.7 \mu\text{m/h}$. Thin (100–1000 Å) undoped ZnTe layer was employed in order to reduce the strong mismatch between $2.0 \mu\text{m}$ thick CdTe buffer layer and GaAs substrate and to stabilize the growth in the [100] direction [2].

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3. Experiment

$\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ layer quality and its chemical composition were determined by X-ray diffraction using $\text{Co } K_\alpha$ radiation. Raman scattering experiments were performed in a quasi-backscattering geometry. Most of the Raman spectra were recorded using a double monochromator equipped with holographic grating and a S20 photomultiplier, some of the spectra were taken using an array of crystalline detectors (a CCD detecting system). Selected Ar^+ (457.9 nm, 476.5 nm and 514.5 nm) and Kr^+ (530.9 nm and 647.1 nm) laser excitation lines and different light polarizations were applied for the measurements (details of the optical setup are described elsewhere [3]).

4. Results and discussion

The lattice parameter changes in a linear manner with the chemical composition for $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ mixed crystals. The rocking curve measurements enable one to determine the value of the lattice parameter as well as the crystal perfection of the layer. Information about the layer quality is given by the value of the full width at half maximum (FWHM) whereas the lattice parameter — by the angular positions of the rocking curves. The rocking curves obtained for the 004 Bragg reflections of two $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ layers are shown in Fig. 1. The accuracy of the chemical composition obtained from such studies is in our case as high as 1%.

Fig. 1. Rocking curves obtained for the 004 Bragg reflections of the (001) $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ layers: (a) $6.3 \mu\text{m}$ $\text{Cd}_{0.34}\text{Mn}_{0.66}\text{Te}/100 \text{ \AA}$ ZnTe/GaAs (the lattice parameter $a_x = 6.387 \text{ \AA}$), (b) $0.2 \mu\text{m}$ $\text{Cd}_{0.10}\text{Mn}_{0.90}\text{Te}/3.0 \mu\text{m}$ $\text{CdTe}/100 \text{ \AA}$ ZnTe/GaAs ($a_x = 6.352 \text{ \AA}$). The lattice parameter is determined from Bragg angle θ_{hkl} given by the formula: $\theta_{hkl} = (\omega_{\min} + \omega_{\max})/2$.

Lattice excitations for $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ mixed crystals consists of two pairs (LO-TO) of modes corresponding to the zone center "MnTe-like" and "CdTe-like" excitations. Frequencies of these excitations depend on the mixed crystal composition. In particular, LO phonon frequency for "MnTe-like" branch changes almost

linearly with an increasing amount of Mn in the layer [4–7]. Thus, such LO frequency value can be also used for the crystal composition determination.

Raman spectra taken for thin $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ slabs exhibit two pairs of sharp lines corresponding to the lattice modes mentioned above. Resulting LO- and TO-frequencies as a function of Mn concentration correspond well to the previously reported data obtained for bulk crystals in the composition range $0 \leq x \leq 0.7$ from the infrared reflectivity [4, 5] and Raman scattering measurements [6, 7]. Slightly non-linear dependence of the “MnTe-like” LO mode on the mixed crystal composition (suggested by a part of the previous data) is confirmed. In particular, optical phonon frequencies for cubic MnTe are directly determined at various temperatures. LO phonon frequency at room temperature equal to about 216 cm^{-1} confirms the only Raman scattering data shown previously in the literature [8]. LO and TO phonon frequencies for cubic MnTe directly determined by our measurements at 17 K equal to $(218 \pm 1) \text{ cm}^{-1}$ and $(190 \pm 1) \text{ cm}^{-1}$, respectively, are in perfect agreement with the values recently determined by the infrared transmission measured with light incident at oblique angles [9].

On the basis of the typical Raman scattering measurements crystal composition can be determined for $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ mixed crystal with an accuracy of about 3%. However, if one applies CCD detector the sensitivity of this method can be much higher. Figure 2a shows a part of the Raman spectrum taken at low temperature for a MnTe slab grown on a thick $\text{Cd}_{0.10}\text{Mn}_{0.90}\text{Te}$ buffer layer. As one can see, two structures corresponding to lattice excitations in the layers mentioned above are very well separated.

For compositions of the mixed crystals close to MnTe an additional, well pronounced structure in the Raman spectra (group of lines in the spectral range from 95 cm^{-1} to 143 cm^{-1}) is observed at every temperature (see Fig. 2b). These lines are identified as corresponding to the crystalline Te precipitates [10]. Crystalline Te due to its trigonal symmetry has three Raman active modes, a supplementary structure could also appear at about 105 cm^{-1} for some Te crystal orientations.

In the case of MnTe for high values of the Te/Mn flux ratio the results of Raman scattering measurements are confirmed by X-ray diffraction studies. Perhaps the number or size of precipitates strongly decreases with an increasing amount of Cd and the crystalline Te was not detected for the sample with the lowest Mn content ($x = 0.66$). Raman scattering is much more sensitive than the typical X-ray diffraction, which was able to detect these precipitates only for a few MnTe samples. More information about Te precipitates in cubic MnTe crystals can be found in [11].

There exists also another advantage of the Raman scattering investigations. It is possible to detect even thin ZnTe layer by X-ray diffraction if this layer is on the top of the structure. Detection of thin ZnTe buffer layers (covered by, e.g., $2.0 \text{ }\mu\text{m}$ thick CdTe buffer layer and a few micrometer thick MnTe layer) by the X-ray diffraction is much more difficult and usually such layers are not seen. On the contrary, Raman scattering can be applied in order to investigate, e.g., ZnTe buffer layers as thin as $100 \text{ \AA}$ (in the case of well chosen laser excitation line Raman scattering process is very effective for ZnTe). Moreover, due to the possible effects of strain (or stress) in the studied layer one can expect a slight shift of ZnTe

Fig. 2. (a) Part of the Raman spectrum taken for 1.0 μm MnTe/1.6 μm $\text{Cd}_{0.10}\text{Mn}_{0.90}\text{Te}/\text{GaAs}$ at 15 K (Kr^+ laser 647.1 nm excitation line). Two peaks correspond to LO phonons for the "MnTe-like" excitation branch for the mixed crystal and MnTe, respectively. (b) Part of the Raman spectrum corresponding to the crystalline Te and MnTe LO-phonon excitations taken for 2.3 μm MnTe/1000 $\text{\AA}$ ZnTe/GaAs at 295 K (Ar^+ laser 476.5 nm excitation line). (c) Part of the Raman spectrum taken for 2.0 μm MnTe/3.0 μm CdTe/200 $\text{\AA}$ ZnTe/GaAs at 17 K (Ar^+ laser 476.5 nm excitation line) corresponding to LO phonon excitations for ZnTe and MnTe. The peak caused by 200 $\text{\AA}$ ZnTe buffer layer is well seen.

LO phonon frequency in comparison to the LO phonon frequency for the bulk material.

ZnTe buffer layers were detected for every investigated sample by the Raman scattering measurements. As an example, part of the Raman spectrum close to ZnTe LO excitation taken at low temperature for one of our samples is shown in Fig. 2c. In particular, small difference in the relative positions of LO modes corresponding to ZnTe and MnTe, respectively, has been observed when analyzing the data taken for various ZnTe slabs with different thickness. Unfortunately, the relative shift of these lines does not exceed 2–3 cm^{-1} , which is comparable to the spectral resolution of our Raman spectrometer and a detailed quantitative analysis of this effect seems to be difficult. ZnTe buffer layer with a thickness probably smaller than 30 $\text{\AA}$ should enable such analysis due to the greater effect expected.

It should be stressed that Raman scattering measurements can be applied in order to study not only thin semiconductor epilayers but also semiconductor quantum wells and superlattices. Usually quantum-size effects and strain effects are experimentally verified by the excitation luminescence measurements (see, e.g., [12] and the references therein), the latter effects can also be observed by X-ray diffraction methods. As it has been mentioned previously the Raman data are sensitive to the possible strain in the structure and this technique is often used, in particular for III-V compounds. Moreover, information about interface roughness and layer thickness fluctuations in superlattices and quantum wells can also be obtained from the analysis of the Raman spectra, as it was shown in [13].

Raman scattering can be used for investigations of the magnetic interactions and the magnetic phase transitions (observation of magnons) but it is a separate problem which is not analyzed in this paper. Some recent data concerning Raman scattering on magnons in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ mixed crystals can be found in [14].

Concluding, we would like to state that Raman scattering is not as precise method as the X-ray diffraction for the determination of the mixed crystal composition, but is very useful when looking for the small amount of other phase in the investigated crystal.

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