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Photoemission spectra of frozen rock salt $\text{Pb}_{1-x}\text{Cd}_x\text{Te}$ crystal

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ABSTRACT

The bulk single crystals of $\text{Pb}_{1-x}\text{Cd}_x\text{Te}$ were obtained by self-selecting vapor growth (SSVG) method with proper quenching. Tunable high energy X-ray photoemission spectroscopy (THE-XPS) and ultraviolet photoemission spectroscopy (UPS) were applied to study the crystals electronic structure of valence band and core level regions. The valence band density of states distribution spectra remarkably changes with the crystal composition. In most cases obtained valence band spectra of ternary crystal with dominating of ionic bonding can be in first approximation treated as a sum of the components spectra. In the case of measured $\text{Pb}_{1-x}\text{Cd}_x\text{Te}$ ternary crystal this first order approximation does not follow the rule and inclination of ternary crystal spectra possesses some differences from the sum of spectra measured for crystal PbTe and CdTe. The increase of Cd contents in the crystals leads to appearance of an additional density of states in the large part of the valence band, for binding energy range up to 10 eV.

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1. Introduction

The PbTe–CdTe system constitutes an attractive material for development of certain electronic or optoelectronic devices. Highly promising case is represented by the quantum dots (QD) of PbTe crated in CdTe matrix for IR detectors. The both crystals PbTe and CdTe are of different crystalline structures and their relative solubility is remarkably low. The PbTe belongs to the group of IV–VI narrow gap (0.23 eV) semiconductor compounds and crystallizes in the six fold coordinated lattice of rock salt type structure, while the CdTe belongs to the group of II–VI middle gap (1.45 eV) semiconductor compounds and crystallizes in four fold coordinated zinc blend type structure. The nucleation of PbTe QD in CdTe is determined by low relative solubility of these materials and the dots size control allows the turning of the quantum dots luminescence over a wide spectral range and this result is a necessity for development of super luminescent diodes operating in the near and mid-infrared regions [1,2].

The other example of PbTe–CdTe system for potential application is $\text{Pb}_{1-x}\text{Cd}_x\text{Te}$ bulk crystal with a high Cd content which can be used for the thermoelectric applications. As it was mentioned above, due to the limited mutual solubility of PbTe and CdTe, resulting from the difference in their crystal structure, growth of uniform

$\text{Pb}_{1-x}\text{Cd}_x\text{Te}$ single crystal with a high concentration of cadmium is the complex task.

The bulk $\text{Pb}_{1-x}\text{Cd}_x\text{Te}$ solid solutions were obtained in the form of polycrystalline samples only, produced mainly by the Bridgman technique or by a rapid quenching followed by annealing [3–6]. In the current work, we present the results of the electronic structure of valence band and core level regions of the frozen rock salt crystals of $\text{Pb}_{1-x}\text{Cd}_x\text{Te}$ grown by physical vapour transport method and proper quenching.

2. Materials and experimental conditions

The bulk single crystals of $\text{Pb}_{1-x}\text{Cd}_x\text{Te}$ were grown in the Institute of Physics, Polish Academy of Sciences in Warsaw by self-selecting vapor growth (SSVG) method which is marked by near equilibrium growth conditions [7]. This method provides most favorable growth conditions, as the growing crystal contacts exclusively with its own source material of the same composition. Moreover, the almost isothermal, closed growth system tends to an increase of entropy with the result in excellent compositional uniformity. This system allows to grow the metastable $\text{Pb}_{1-x}\text{Cd}_x\text{Te}$ crystals in the temperature range of stability with rapid cooling to freeze the high-temperature phase existing between the solidus line and the bottom temperature of stability known from the published phase diagram [3]. The structural, electrical and optical properties were studied experimentally and theoretically [8,9]. Crystals of about 1 cm volume with (001) natural

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Fig. 1. The set of valence band EDCs for different $\text{Pb}_{1-x}\text{Cd}_x\text{Te}$ crystal compositions. The excitation energy: $h\nu = 50$ eV.

facets were obtained with FWHM rocking curve values of below 2 arcmin and almost absolutely uniform composition in respect to the CdTe molar fraction x . The study of X-ray diffraction of $\text{Pb}_{1-x}\text{Cd}_x\text{Te}$ ternary crystal performed at room temperature confirms a single-phase rock-salt solution.

The compositions of the input materials prepared for the growth of the investigated crystals were set with $x = 0.06, 0.08$ and 0.15 by use of CdTe–PbTe mixtures as weighed starting materials. However, the sample compositions assessed by energy dispersive X-ray spectroscopy (EDX) turned out to be $x = 0.01, 0.015$ and 0.08 , respectively (the difference between the weighed compositions and the obtained crystals requires closer study of crystal growth conditions). The components of the crystals were distributed uniformly within the limits of the lateral resolution of EDX. The crystal composition measurements were carried out with use of the Hitachi SU-70 scanning electron microscope equipped with the EDX system with Thermo Scientific UltraDry silicon drift detector and Noran System 7 X-ray microanalysis equipment.

The photoemission studies were performed at room temperature with application of the synchrotron radiation in the HASYLAB, DESY, Hamburg, Doris III storage ring. The spectra were normalized to the radiation beam intensity. The clean crystal surface was obtained by argon ion sputtering and annealing under UHV conditions.

The tunable high energy X-ray photoemission spectroscopy (THE-XPS) experiment was performed at wiggler beam line sta-

Fig. 2. HE-XPS spectra of $\text{Pb}_{0.94}\text{Cd}_{0.06}\text{Te}$ single crystal for different regions: (a) the valence band and the Cd4d, Pb5d, Te 4d core levels; (b) the Pb 4f core level; (c) the Pb 4d and Cd 3d core levels; (d) the Te 3d core level. The excitation energy: $h\nu = 3510$ eV. The solid lines (a–c) and dots (d) correspond to the experimental results, the dashed lines – the background calculated by the Shirley method, the dot curve (d) the Voigt maxima fitted to the experimental results.

tion BW2. Double crystal Si(1 1 1) monochromator covers an energy range from 2.4 to 10 keV with a monochromatic photon flux of about 5×10^{12} photons/s and with total energy resolution power of 0.5 eV for radiation energy around 3000 eV. The total energy resolution was kept at 0.1 eV for THE-XPS. The origin of the energy axis was set at the Fermi energy as measured for a reference Au sample [10].

The ultraviolet photoemission spectroscopy experiments were performed at beam line station FLIPPER II. Synchrotron radiation obtained from the storage ring DORIS III was monochromatized with the plane grating vacuum monochromator designed for the photon energy range of 15–200 eV. The spectrometer was equipped with a CMA electron energy analyzer and the energy resolution was kept at 0.2 eV for UPS spectra.

3. Results and discussion

Fig. 1 shows the set of EDCs taken at the excitation energy of 50 eV for $\text{Pb}_{1-x}\text{Cd}_x\text{Te}$ crystals with different Cd contents equal $x = 0.01, 0.015$ and 0.08 . The spectra cover the valence band region and the Cd 4d level and they were normalized to the light intensity and scan numbers. As it can be seen in the figure, the increase of Cd contents in the crystals (x – indicated on the figure) leads to appearance of remarkable changes of the density of states in the large part of the valence band region, for binding energy range from 3 to 10 eV, as well as for the peak related to Cd 4d electrons with the binding energy of 11.8 eV. In most cases valence band spectra of ternary crystals with dominating ionic bonding can be in the first approximation treated as a sum of the components spectra. The investigated $\text{Pb}_{1-x}\text{Cd}_x\text{Te}$ ternary crystals do not follow this rule and ternary crystal spectra markedly deviate from the sum of spectra measured for PbTe and CdTe [11]. These results show that the grown frozen rock salt crystals of $\text{Pb}_{1-x}\text{Cd}_x\text{Te}$ possess modified density of states distribution in the valence band.

The THE-XPS spectra of $\text{Pb}_{0.99}\text{Cd}_{0.01}\text{Te}$ single crystal are presented in Fig. 2. The spectra were taken for the binding energy regions corresponding to emission from the Cd 4d, Pb 5d, Te 4d, Pb 4f, Pb 4d, Cd 3d, and Te 3d core levels. The excitation energy was equal to 3510 eV. As it can be seen from the spectrum the Pb 5d spin–orbit doublet is located at 18.67 and 21.33 eV. These results correlate with results obtained for PbTe single crystals using monochromatized Al $K_{\alpha 1,2}$ radiation source [12]. The XPS spectrum with Cd content $x = 0.06$ (Fig. 2a) does not deviate much from XPS spectrum of pure PbTe [12]. Between the Pb 5d lines and the valence band exist two less intensive peaks labeled as 1 (8.39 eV) and 2 (11.19 eV) (see Fig. 2a). These peaks are identified as arising from Pb 6s and Te 5s orbitals respectively [11,12]. The 2–1 peaks splitting is 2.8 eV in our crystal and is equal 3.5 eV in PbTe. The comparison of the peak positions and intensities in the spectra of $\text{Pb}_{0.99}\text{Cd}_{0.01}\text{Te}$ with those of pure PbTe shows that the increase of Cd contents has modified strongly the density of states distribution in the valence band region.

In Fig. 2b the spectrum of the Pb 4f level is shown. The spin–orbit splitting between the Pb $4f_{7/2}$ and Pb $4f_{5/2}$ maxima is equal to 4.92 eV. The intensity ratio of 1.23 corresponds reasonably well to the multiplicity ratio of the components.

Fig. 3. HE XPS Te 3d core level spectrum of $\text{CdTe}/\text{Pb}_{0.95}\text{Eu}_{0.05}\text{Te}/\text{CdTe}$ heterostructure. The excitation energy: $h\nu = 3510$ eV. The dots correspond to the experimental results, the dashed line to the background calculated by the Shirley method, and the dot curve to the Voigt maxima fitted to the experimental results.

The THE-XPS spectrum of $\text{Pb}_{0.99}\text{Cd}_{0.01}\text{Te}$ single crystal for Pb 4d and Cd 3d core levels region is presented in Fig. 2c. The large Pb $4d_{5/2}$ signal partly overlaps the Cd 3d core level. The Cd $3d_{5/2}$ peak appears as a small peak (in good agreement to the relatively small Cd atoms contribution in the crystal) at the binding energy equal to 404.95 eV.

The THE-XPS spectrum of $\text{Pb}_{0.99}\text{Cd}_{0.01}\text{Te}$ single crystal for Te 3d core level region is presented in Fig. 2d. The Te 3d spectrum consists of spin–orbit doublet at 582.48 eV and 571.94 eV respectively. The spectrum was satisfactorily fitted with two Voigt singlets centered at 571.94 eV and 582.48 eV with FWHM of 0.89 eV and 0.88 eV for Te $3d_{5/2}$ and Te $3d_{3/2}$, respectively. The curve taken for $\text{Pb}_{0.99}\text{Cd}_{0.01}\text{Te}$ can be compared with a typical THE-XPS Te 3d core level spectrum of $\text{CdTe}/\text{Pb}_{0.95}\text{Eu}_{0.05}\text{Te}/\text{CdTe}$ heterostructure (Fig. 3). The experiment for this system was performed at the same beam-line station as in the case of $\text{Pb}_{0.94}\text{Cd}_{0.06}\text{Te}$ single crystal and for the same excitation energy of 3510 eV. The obtained spectrum can also be fitted two Voigt profiles centered at 572.02 eV and 582.57 eV with FWHM of 1.16 eV and 1.17 eV. The larger width of the lines observed for $\text{CdTe}/\text{Pb}_{0.95}\text{Eu}_{0.05}\text{Te}/\text{CdTe}$ may indicate that different contributions from CdTe and $\text{Pb}_{0.95}\text{Eu}_{0.05}\text{Te}$ form the observed features although they cannot be resolved in the spectra. In spite of the chemical disorder and the presence of Te ions with different surroundings in the solid solution, the Te 3d maxima are markedly narrower for $\text{Pb}_{0.99}\text{Cd}_{0.01}\text{Te}$. No features that could be related to separated phases has been resolved in the spectra.

The binding energies measured by XPS for the main lines for $\text{Pb}_{0.99}\text{Cd}_{0.01}\text{Te}$ single crystal and for $\text{CdTe}/\text{Pb}_{0.95}\text{Eu}_{0.05}\text{Te}/\text{CdTe}$ heterostructure are presented in Table 1. The Cd $3d_{5/2}$ binding energy value in the single crystal is very close to the binding energy of Cd $3d_{5/2}$ peak in CdTe [13] and $\text{CdTe}/\text{Pb}_{0.95}\text{Eu}_{0.05}\text{Te}/\text{CdTe}$ heterostructure.

Table 1

XPS measured binding energies (in eV) for core levels of components of $\text{Pb}_{0.94}\text{Cd}_{0.06}\text{Te}$ single crystal and for $\text{CdTe}/\text{Pb}_{0.95}\text{Eu}_{0.05}\text{Te}/\text{CdTe}$ heterostructure.

Sample	Core level						
	Pb $5d_{5/2}$	Pb $4f_{7/2}$	Pb $4d_{5/2}$	Cd 4d	Cd $3d_{5/2}$	Te $4d_{5/2}$	Te $3d_{5/2}$
$\text{CdTe}/\text{Pb}_{0.95}\text{Eu}_{0.05}\text{Te}/\text{CdTe}(100)$	18.45	137.18	–	10.91	404.85	39.87	572.02
$\text{Pb}_{0.94}\text{Cd}_{0.06}\text{Te}$	18.67	137.32	412.19	–	404.95	39.86	571.94

4. Summary and conclusions

The valence band of PbTe and $\text{Pb}_{1-x}\text{Cd}_x\text{Te}$ ($x=0.01, 0.015$ and 0.08) samples were investigated by photoemission spectroscopy with use of synchrotron radiation for the photon energy range of 45–60 and 3510 eV.

The increase of Cd contents in the crystals leads to the appearance of an additional density of states in the large part of the valence band, for binding energy range from 3 to 10 eV. This set of curves is planned to be compared with the tight binding calculation of ternary crystal band structure [8].

The experiments show that a solid solution has been created with strongly modified density of states distribution in the valence band. The analysis of the core level spectra of $\text{Pb}_{0.99}\text{Cd}_{0.01}\text{Te}$ shows no features related to phase separation in the system.

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