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Photoemission Electronic Spectra of CdTe/$\mathbf{Pb_{0.95}Eu_{0.05}}$Te/CdTe

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The synchrotron radiation was used to apply tunable high energy X-ray photoemission spectroscopy for investigation of electronic structure of semiconductor nanostructure CdTe/$Pb_{0.95}Eu_{0.05}$Te/CdTe/GaAs(001) top part. The $Pb_{0.95}Eu_{0.05}$Te (6 nm thick) was buried under thin (22 nm) top layer of CdTe transparent for part of electrons photoemitted from $Pb_{0.95}Eu_{0.05}$Te buried layer. The top layer of CdTe was sputtered by Ar ion bombardment for surface cleaning and for leaving the thickness of CdTe more transparent for photoelectrons emitted from buried layer. For these thickness of the top layer the photoemission energy distribution curves corresponding to the valence band and core levels electrons of the buried layer atoms were measured with application of synchrotron radiation of energy $h\nu = 3510$ eV. The measured spectra corresponding to the buried layer atoms were observed in the valence band region and in the high binding energy region for core levels of Pb $4f$, Pb $3d$. The valence band contribution and core levels Cd $4d$ and Cd $3d$ were obtained mainly from top cover layer. Measured Te $4d$, Te $3d$ and Te $4d$ spectra possess contribution as well from top cover layer as from the buried layer. The amount of Eu atoms was to small to be reasonable detected and presented in the paper.

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1. Introduction

Semiconductor materials like tellurides of lead and cadmium are intensively investigated and applied as well for optoelectronics — optical detectors and emitters, as in magnetic and thermoelectric devices. In last decade the nanostructures with a quantum dots made of these materials are of great interest for research and application. The very promissible case is represented by the quantum dots of PbTe created in between the layers of CdTe [1–4]. The both crystals PbTe and CdTe are of different crystalline structure and their relative solubility is remarkably low. Due to low relative solubility the small islands of PbTe grown between CdTe layers after heating do not inter-diffuse and do not create ternary alloy of PbCdTe but PbTe islands precipitate in the shape of dots. The PbTe belongs to the group of IV–VI narrow gap (0.23 eV) semiconductor compounds and crystallizes in the sixfold coordinated lattice of rocksalt (lattice constant 6.462 Å) while the CdTe belongs to the group of II–VI middle gap (1.45 eV) semiconductor compounds and crystallizes in fourfold coordinated zinc blende lattice (lattice constant 6.480 Å). The nanostructures are frequently grown by the molecular beam epitaxy (MBE) deposition. The PbTe layer grows on the buffer layer of CdTe as islands. The next layer of the nanostructure is CdTe top layer. During annealing of the sample the PbTe islands located between CdTe layers change into the PbTe isolated quantum dots. The dots are nearly regularly distributed in the plane between CdTe layers and their diameter increases with increase of thickness of deposited PbTe layer [1, 2]. The dots of CdTe were also obtained in the structure like PbTe/CdTe/PbTe nanostructure.

The effort was done to introduce Eu atoms to the dots of PbTe created in between CdTe layers by MBE deposition. It was expected that the high energy photoemission spectra will allow us to investigate electronic structure of buried dots or islands of PbTe doped with Eu due to high escape depth of the electrons photoemitted from buried layer.

2. The sample preparation and experiment

The nanostructure was grown by MBE deposition method in the Institute of Physics, Polish Academy of Sciences in Warsaw [3, 4]. Independent Knudsen cells were used to deposit CdTe, PbTe, Te, and Eu to grow the nanostructure. Set of performed experiments gave the possibility to grow proper size of deposited layer of PbTe and proper lowest thickness of CdTe cap layer to obtain PbTe dots. The CdTe buffer layer was deposited on GaAs wafer and $Pb_{0.95}Eu_{0.05}$Te layer of 6 nm thickness was evaporated on it. The number of Eu atoms in deposited layer was to small to be accurately detected and are not presented in the paper.

The layer of $Pb_{0.95}Eu_{0.05}$Te was covered by CdTe top layer of thickness 22 nm. It was thick enough top layer to obtain transition of deposited islands and dots of the layer of $Pb_{0.95}Eu_{0.05}$Te. Contribution of Eu atoms did not disturb transition of islands of layers in dots. Microscopic studies of the cleavage of the nanostructure

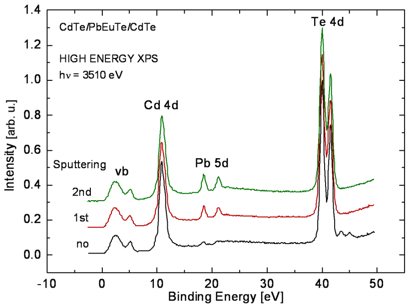

Fig. 1. Set of EDC's of the valence band region and Cd $4d$, Te $4d$ electrons measured after following steps of cleaning of the sample by sputtering part of CdTe 22 nm cup layer to lower thickness down to about 7 nm.

showed the existence of dot as well as islands of buried layer. The nanostructure was exposed to air and photoemission spectra were performed *ex situ* on line station BW2 at HASYLAB. The experiment was performed using the tunable high energy X-ray photoemission spectrometer (THE-XPS) at wiggler beam line station BW2 of the HASYLAB, DESY, Hamburg, Doris III storage ring [5]. Double crystal monochromator with crystal Si(111) works in the energy range from 2.4 to 10 keV with photon flux of about 5×10^{12} photons/s of monochromatic beam and with total energy resolution power of 0.5 eV for radiation energy around 3000 eV. The station is adopted to perform the experiment with high-energy X-ray photoelectron spectroscopy. The photoemission studies were performed at room temperature. In previous experiment [6, 7] the energy $h\nu = 3510$ eV was found as an optimal for the measurements of EuS layer buried in PbS. The set of measured spectra contains: valence band, Cd $3d$ and $4d$, Pb $4f$ and $5d$ and Te $3d$ and $4d$ electrons. The big thickness of CdTe layer (22 nm) covering $Pb_{0.95}Eu_{0.05}Te$ layer was strongly damping the electrons emitted from the layer. After Ar ion sputtering of CdTe top layer, the photoemission signal corresponding to Pb $5d$ electrons of buried layer remarkably increases. Figure 1 presents the set of energy distribution curves (EDC's) of the valence band region and Cd $4d$, Pb $5d$ and Te $4d$ core levels electrons measured after sequential steps of sputtering part of CdTe 22 nm cap layer to lower thickness of it down to about 7 nm.

The Ar ion sputtering of the top CdTe layer is expected to be destructive for the CdTe layer and in microscale the thickness of the cover layer of CdTe can be changed along the layer. It will lead to the difficulties to estimate cap layer thickness and to correlate it to the relative change of structures of the measured photoemission spectra. Taking into account the changes of Pb $5d$ peak height relatively to Cd $4d$ peak height we roughly estimated approximate values of escape depth of the electrons photoemitted from Pb $5d$ through CdTe cap layer as being in the range of about 6 ± 2 nm.

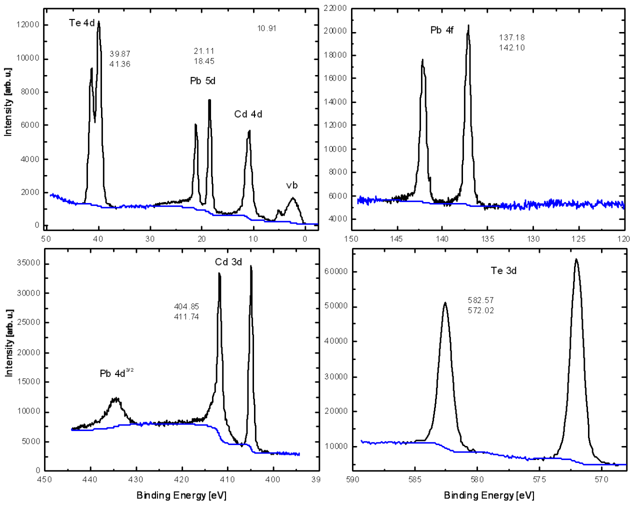

Fig. 2. THE-XPS spectra of CdTe/PbEuTe/CdTe/GaAs nanostructure for different binding energy regions: (a) valence band and Cd $4d$, Pb $5d$, Te $4d$ core levels; (b) the Pb $4f$ core level; (c) the Pb $4d$ and Cd $3d$ core levels; (d) the Te core level. The excitation energy 3510 eV. The solid lines correspond to the measured curves, the dashed lines — to the background calculated by the Shirley method.

Figure 2 presents the spectra of valence band region (a) and the core levels electrons corresponding to the nanostructure components. Presented peaks (Fig. 2) are characterized by the value of the binding energies corresponding to the single or spin–orbital split peaks. All of these values of the core levels binding energies are indicated in Table. The measured spectra well correspond to the spectra presented in the papers [8, 9].

Let us compare the tendency of the binding energy differences of cation Pb $5d$ and $4f$ electrons and anion Te $3d$ and $4d$ electrons obtained for the case of $Pb_{0.94}Cd_{0.06}Te$ frozen crystal (obtained by the rapid cooling to freeze the high temperature phase existing between the solidus line and the bottom temperature of stability [10]) and $Pb_{0.95}Eu_{0.05}Te$ nanostructure grown in thermodynamic equilibrium in MBE system. In ionic crystal each investigated ion is located in the point where the electrostatic potential is created by the ligands and other surrounding ions of the crystal. The change of these potential is causing the change of the photoemitted electrons binding energy. These electrostatic potential can be changed when the position of the ligands and/or surrounding ions will be changed.

The electrostatic potential decreases when the distance between investigated ion and ligands and other surrounding ions of the crystal increases. It leads to the increase of the electrons binding energy of investigated anion and to decrease of electrons binding energy of investigated cation.

TABLE

THE-XPS measured binding energies for core level components of $Pb_{0.94}Cd_{0.06}Te$ [10] single crystal and for $CdTe/Pb_{0.95}Eu_{0.05}Te/CdTe/GaAs$ heterostructure. Corresponding data for Cd, Pb and Te taken from [11].

Sample	Core level [eV]						
	Pb $5d_{5/2}$ Pb $5d_{3/2}$	Pb $4f_{7/2}$ Pb $4f_{5/2}$	Pb $4d_{5/2}$ Pb $4d_{3/2}$	Cd $4d_{3/2}$ Cd $4d_{1/2}$	Cd $3d_{5/2}$ Cd $3d_{3/2}$	Te $4d_{5/2}$ Te $4d_{3/2}$	Te $3d_{5/2}$ Te $3d_{3/2}$
$CdTe/Pb_{0.95}Eu_{0.05}Te/CdTe(100)$	18.45	137.18	–	–	404.85	39.87	572.02
	21.11	142.10	435.50	10.91	411.85	41.36	582.57
$Pb_{0.94}Cd_{0.06}Te$	18.67	137.32	412.19	–	404.95	39.86	571.94
	21.33	142.24	434.67	11.19	–	41.34	582.48
Cd				10.7	405.2		
				11.7	411.9		
Pb	18.1	136.9	412.2				
	20.7	141.7	434.3				
Te						40.4	573.0
						41.9	583.4

In frozen ternary crystal $Pb_{0.94}Cd_{0.06}Te$ the binding energy of cation Pb 5*d* and 4*f* electrons have a tendency to be bigger value (see Table) than for the same ion electrons but located in nanostructure $Pb_{0.95}Eu_{0.05}Te$ grown in thermodynamic equilibrium. The opposite relation appears for anion Te 3*d* and 4*d* electrons where the binding energy have tendency to the lower value of binding energy in ternary frozen crystal $Pb_{0.94}Cd_{0.06}Te$ (see Table) than in $Pb_{0.95}Eu_{0.05}Te$ nanostructure. Introduction of ion Cd (radius 0.97 Å) on the seat of ion Pb (radius 1.20 Å) leads to the collapse of the (Te ions) around introduced Cd. In the crystal it will create local structure and it will lead to the increase of Pb–Te distance of the Cd ion nearest ligands in the frozen ternary crystal $Pb_{0.94}Cd_{0.06}Te$. The increase of Pb–Te distance leads to the decrease of the electrostatic potential in the point where Pb ion is located and it will cause the increase of observed binding energy of Pb 5*d* and 4*f* electrons in $Pb_{0.94}Cd_{0.06}Te$ frozen ternary crystal. The opposite relation of the binding energy shift will appear for binding energy of Te 3*d* and 4*d* electrons where the increase of Pb–Te distance leads to the increase of the electrostatic potential in the point where Te ion is located and it will cause binding energy decrease observed for Te 3*d* and 4*d* electrons in frozen ternary crystal.

We can conclude that discussed shifts of binding energy are correlated to the local structure effects presented in the frozen ternary crystal $Pb_{0.94}Cd_{0.06}Te$.

3. Summary

The nanostructures of $CdTe/Pb_{0.95}Eu_{0.05}Te/CdTe/GaAs(100)$ were grown by the MBE deposition from the four Knudsen cells of CdTe, PbTe, Te and Eu. Microscopic study of the grown nanostructure showed that PbTe dots can be created and that the dots are doped by europium atoms and the atoms did not disturb creation of dots. The experiment was performed *ex situ* for cleaned top layer of nanostructure and the THE-XPS with excitation energy $h\nu = 5310$ eV. The set of measured spectra contain: valence band and core levels Cd 3*d* and 4*d*, Pb 4*f* and 5*d*, Te 3*d* and 4*d*. The measured values of binding energies are presented in Table. The observed tendency to increase of Pb 5*d* and 4*f* electrons binding energy and to decrease of Te 3*d* and 4*d* binding electrons for investigated two samples well correlate to the appearance of local structure in $Pb_{0.94}Cd_{0.06}Te$ ternary alloy.

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