Nuclear Instruments and Methods in Physics Research B 364 (2015) 132–135

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

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

Synchrotron radiation photoemission study of $Pb_{1-x}Cd_xTe$ crystal with local structure

B.A. Orlowski [a,*], A. Szczerbakow [a], P. Dziawa [a], K. Gas [a], A. Reszka [a], B.J. Kowalski [a], S. Thiess [b], W. Drube [b]

[a] Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 32/46, 02-668 Warsaw, Poland
[b] Hamburger Synchrotronstrahlungslabor HASYLAB am DESY, Notkestr. 85, D-22603 Hamburg, Germany

ARTICLE INFO

Article history:
Received 17 September 2014
Received in revised form 17 June 2015
Accepted 21 June 2015
Available online 4 July 2015

Keywords:
Semiconductor ternary alloy
Photoemission
Local structure

ABSTRACT

The paper presents photoemission study of core level binding energy shifts caused by local crystalline structure collapse in cubic $Pb_{1-x}Cd_xTe$ crystal. Photoemission spectra of two kinds of semiconductor samples are compared. The first one is ternary crystal of $Pb_{0.94}Cd_{0.06}Te$ with the frozen rock salt structure where the crystalline local structure collapse is expected due to the difference of ion radii of Cd and Pb cations. The second sample was the CdTe(22 nm)/PbTe(6 nm)/CdTe(4 μm)/GaAs(1 1 1)B nanostructure grown by molecular beam epitaxy (MBE) method, where crystalline local structure is not expected to be created. The photoemission spectra show that for the crystal with local structure the electron binding energies of cations are higher (e.g. +0.2 eV) whereas for anions they are lower (e.g. −0.08 eV) than in the multilayer structure. A model is proposed to explain obtained results by the local crystalline structure collapse in $Pb_{0.94}Cd_{0.06}Te$ crystal.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Lead and cadmium tellurides are intensively investigated and widely applied semiconductor materials as well in optoelectronics (e.g. in optical detectors), as in electronic and thermoelectric devices. The crystals of PbTe and CdTe are of different crystalline structure and their relative solubility is remarkably low [1]. PbTe belongs to the group of IV–VI narrow gap (0.32 eV at $T = 300$ K) semiconductor compounds and crystallizes in the sixfold coordinated lattice of rock salt (lattice parameter 6.462 Å) while CdTe belongs to the group of II–VI middle gap (1.44 eV at $T = 300$ K) semiconductor compounds and crystallizes in fourfold coordinated zinc blend lattice (lattice parameter 6.480 Å). The low solubility of PbTe and CdTe results in quantum dots formation of either PbTe in CdTe or CdTe in PbTe when a ternary alloy is attempted to grow by MBE method. This system is of a great interest both for basic research and applications [2–5]. The $Pb_{1-x}Cd_xTe$ phase diagram does not permit growth of the crystals with $x > 0.03$ from the melt by most of routine growth methods. However, the self-selecting vapor growth (SSVG) method, which is based on near equilibrium growth conditions [1], allows us to obtain relatively large cubic $Pb_{1-x}Cd_xTe$ ternary crystals of high structural quality in the composition range up to $x = 0.1$ with frozen rock salt structure [2–5].

2. Experiment and results

The bulk single crystals of $Pb_{1-x}Cd_xTe$ with the rock salt structure used for this study were grown by modified SSVG method [1]. The X-ray diffraction study has confirmed the single-phase rock-salt structure without any features indicating a phase separation in the crystalline structure. The lattice parameter of the crystals, as measured by XRD, decreases with the increase of x approximately following the Vegard's law [2]. However, the difference of the ionic radii of Pb^{2+} (1.2 Å) and Cd^{2+} (0.97 Å) should lead to local collapse of the crystalline lattice structure around Cd site in the crystal of $Pb_{1-x}Cd_xTe$. Such a feature is referred to as "local structure". So, at the atomic scale the virtual crystal approximations of average lattice constant cannot be applied.

In the MBE grown multilayer structure, the continuous regions of CdTe and PbTe are separated and a uniform solid solution is not formed [1–5]. The layered structure was grown at 270 °C. First, 4 μm thick CdTe buffer layer on (1 1 1)B oriented GaAs monocrystalline substrate was deposited in a separate MBE system. In the second MBE system binary CdTe and PbTe as well as molecular Te_2 were used as solid sources. After annealing at around 300 °C, refreshing with thin CdTe layer was done. Subsequently, 6 nm thick PbTe layer and finally 22 nm thick CdTe cap layer were grown. During the photoemission experiments the 22 nm of CdTe cap layer was partially removed by argon ion bombardment during surface cleaning procedure. It aloud to obtain spectra from covered PbTe layer. Despite of different crystal structures of CdTe and PbTe

* Corresponding author.

http://dx.doi.org/10.1016/j.nimb.2015.06.021
0168-583X/© 2015 Elsevier B.V. All rights reserved.

(zinc blende and rock salt respectively) the lattice parameter difference is very small (a(PbTe) = 6.462 Å) and (a(CdTe) = 6.480 Å) and the lattice mismatch equals to 0.3%. We will assume that the crystal local structure does not occur in this system.

The photoemission binding energies of core level electrons of $Pb_{0.94}Cd_{0.06}Te$ crystal components (with expected local crystal structure) are compared in the paper with corresponding binding energies of nanostructure layer system (without local structure). Obtained chemical shift of the levels is treated as corresponding to the local change of the distance between the nearest neighbors in the region of the local lattice collapse around the Cd^{2+} ions replacing Pb^{2+} ions in the crystal.

The high energy photoemission experiment was performed using the Tunable High Energy X-ray Photoemission Spectrometer (THE-XPS) at wiggler beam line station BW2 of the Doris III synchrotron storage ring in HASYLAB, Hamburg. Double crystal monochromator with Si(1 1 1) crystals works in 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 of 0.5 eV for radiation energy around 3000 eV. The photoemission studies were performed at room temperature. The Fig. 1 presents the comparison of the sets of couples of photoemission spectra of Cd 4d, Pb 5d, Pb 4f, Te 4d and Te 3d obtained for the crystal and the MBE layer respectively. The energy analyzing system gave the possibility to obtain shift of the shoulder and peak positions with accuracy range of approximately 0.1 eV.

The set of spectra presented in Fig. 1 was obtained keeping the both samples in the same experimental conditions. Thus electron binding energies of the valence band, cations Cd (4d) and Pb (5d, 4f), and anion Te (3d, 4d) were determined for both samples at the same conditions. Obtained electrons binding energies values are presented in Table 1.

3. Model of local structure

Let us consider how the measured binding energies of the cation and anion (Table 1, row 1 for the crystal and row 2 for the multilayer structure) and their differences (Table 1 row 3) correspond to the expected change of nearest neighbor distance appearing in the region of the local crystalline structure.

The local structure model is illustrated in Fig. 2. Fig. 2a presents (1 0 0) plane of $Pb_{1-x}Cd_xTe$ cubic lattice before collapse (left) and after collapse (right) around the Cd cation. It presents the collapse of the PbTe lattice by the shift of the neighboring Te and Pb atoms towards the Cd one. It leads to the creation of the local crystal structure around Cd ion. There is a question, how the additional empty space appearing in the region of lattice distortion will influence the distance of Cd–Te and Pb–Te pairs. What kind of change in the ions distances (increase or decrease) would be consistent with the photoemission experimental data showing simultaneous increase of the cation electrons binding energies together with decrease of the anion electrons binding energies?

Let's take one-dimensional chain of the PbTe, PbCdTe and CdTe presented in Fig. 2b. The top row of the figure represents PbTe clean crystal chain whereas the bottom one represents CdTe crystal chain. The middle row corresponds to the mixed crystal with one Cd ion substituting Pb ion and illustrates how the one-dimensional structure of the chain changes locally and creates local structure around the Cd ion. The Te ions nearest to the introduced Cd ion shift closer to the Cd ion without reaching Cd–Te distance in the CdTe chain. The movement of the Te ions towards the Cd ion leads to increase of distance between these Te ions and their neighboring Pb ions. As a result we obtain new local structure around the Cd ion. In this region both distances between Cd–Te and Pb–Te ions increase respectively to those distances in their parent CdTe and PbTe chains.

Let's compare the binding energy of Cd^{2+} 4d electron for the isolated ion in the vacuum (the third ionization energy is equal to 37.48 eV for Cd atom) with the case when the ion is located in the site of the Pb^{2+} ion in PbTe crystal. As it has been measured in photoemission experiments, this binding energy is reduced to 11.19 eV (see Table 1). This is due to electrostatic potential created at Cd^{2+} sit by surrounding ions of PbCdTe crystal (as the nearest neighbors are negative Te^{2-} ions, the created potential lowers the value of Cd^{2+} 4d electron binding energy by about 20.29 eV (corresponding to the Madelung Energy [6] for ionic crystal, 20.29 eV = 37.48 eV − 11.19 eV − 6 eV (6 eV corresponds to an approximate work function)). Any increase of the nearest neighbor distance will change of the potential and will reduce influence of crystal ions on the binding energy of Cd^{2+} 4d electrons. It will lead to the increase of Cd^{2+} 4d electron binding energy (shift forward to the value 37.48 eV of an isolated ion in vacuum). The increase of the Cd–Te or Pb–Te distances will lead to the increase of the cation electrons binding energy. The analogical consideration can be done for binding energy change of electrons of Te anions. The increase of the nearest neighbor distance of Te ion will lead to the opposite change of the anion electron binding energy (as the nearest neighbors are positive Pb^{2+} or Cd^{2+} ions). In this case, increase of the nearest neighbors distance leads to the decrease of nearest neighbors potential of anion electrons, and it leads to the decrease of the anion electrons binding energies.

Model of cation–anion distance changes presented in Fig. 2b well explains the observed changes of chemical shifts for cation and anion electrons. It shows that in the local structure collapse region the distance between Pb–Te increases relatively to this distance which is out of collapse region of PbTe crystal (compare middle and upper row of Fig. 2b). As well the distance between Cd–Te increases relatively to this distance in CdTe crystal (compare the middle and lowest row of Fig. 2b). The change of the distance between the investigated ion and its nearest neighbors leads to the change of potential created in the site of investigated ion. Those changes will cause the change of binding energy of electron photoemitted from the investigated ion. For the case of cation it leads to the increase of binding energies of electrons of cations Pb^{2+} and Cd^{2+} (as Te^{2-} ion moves away from the cation) while in a case of anion Te^{2-} it leads to the decrease of electron binding energies (as Pb^{2+} and Cd^{2+} ions also moves away from the anion). The distance between Cd–Te also increases (in comparison to that in CdTe crystal) and it leads to the increase of binding energies of electrons in Cd^{2+} ion and to the decrease of binding energy of electrons of Te^{2-} anion (see the lowest row in Table 1). We can conclude that obtained changes of the chemical shifts (see Table 1, the lowest row) well correlate with the changes of distances between the ions in the local structure collapse region postulated in presented model.

The distances of Pb–Te and Cd–Te ions increase and the electron binding energies of Pb^{2+} and Cd^{2+} ions are higher for the crystal with the frozen rock salt structure than for the layered structure grown by MBE. Increase of the distance between cation and anion leads to the decrease of influence of the surrounding crystal on the electron binding energy in the ions. In this case, the binding energies of electron will shift closer to the binding energies of isolated ions. For ions located in the crystal it will cause increase of cation electrons binding energy and decrease of anion electrons binding energy [6–8]. Thus, the obtained electron binding energy differences can be caused due to crystal local structure created in crystalline solid solution $Pb_{0.94}Cd_{0.06}Te$.

Let's consider the expected influence of valence band electrons screening effect on the change of the core electron binding energy of anions or cations. In the crystal of high partial ionic bonding the

Download English Version:

https://daneshyari.com/en/article/8040010

Download Persian Version:

https://daneshyari.com/article/8040010

Daneshyari.com