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National Academy of Sciences of Ukraine***Yurchenko O.M., Piskach L.V.***Lesya Ukrainka Eastern European National University***SINGLE CRYSTAL GROWTH
AND XPS CHARACTERIZATION OF Tl_4HgI_6**

Thallium mercury iodide, Tl_4HgI_6 , is a representative of a fascinating family of the A_4BX_6 compounds attracting great interest from scientific and technological viewpoints due to interesting nonlinear optical properties [1-3]. Tl_4HgI_6 is a direct band gap semiconductor [4] with band gap energy $E_g = 2.15$ eV [5]. In the present work we report on successful synthesis of Tl_4HgI_6 single crystals and their characterization employing possibilities of X-ray photoelectron spectroscopy (XPS). The XPS valence-band and core-level spectra were measured for the Tl_4HgI_6 single crystals grown by Bridgman-Stockbarger technique. In order to obtain large Tl_4HgI_6 single crystals, calculated amounts of purified binary iodides (100 g in total weight) were placed in a growth container, a quartz ampoule of 18 mm inner diameter with a conical bottom. The Tl_4HgI_6 synthesis was made in a single-zone furnace by heating the container with the batch with a rate of 20 K/h at 820 K. The ampoule was kept at this temperature for 10 h, following by its removing from the furnace, cooling to room temperature and transferring to a special container, which was placed in a two-zone growth furnace with constant temperature profile. The growth conditions were selected as following: the temperature of growth zone / annealing zone was set to be 700 K/573 K and the rate of crystallization was 0.5 mm/h. After the completion of the crystallization, annealing was carried out over 120 h followed by very slow (5 K/hr) cooling to room temperature. Fig. 1 demonstrates a photo of as-grown Tl_4HgI_6 single crystal used in the present XPS studies.

**Fig. 1. Photo of as-grown Tl_4HgI_6 single crystal**

Fig. 2 presents the survey XPS spectrum of the pristine surface of the Tl_4HgI_6 single crystal. The XPS measurements were performed with the UHV-Analysis-System produced by SPECS Company (Berlin, Germany).

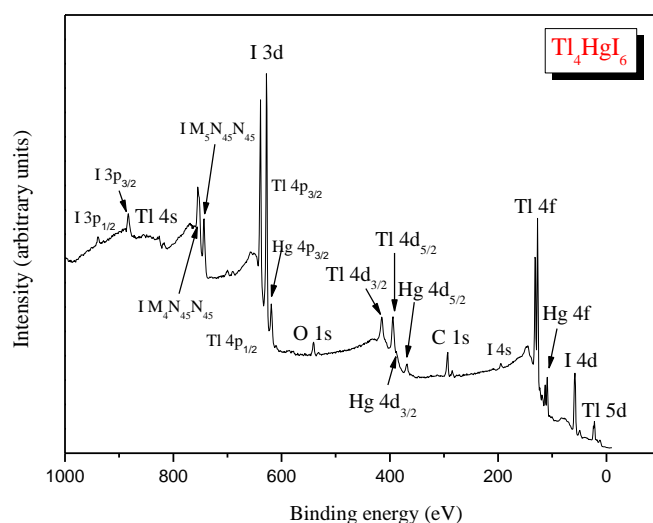


Fig. 2. Survey XPS spectrum of pristine surface of the Tl_4HgI_6 single crystal

The XPS valence-band and core-level spectra of the Tl_4HgI_6 crystal were measured at the base pressure below 9×10^{-10} mbar. The spectra were excited with Mg K_α source of X-ray irradiation ($E=1253.6$ eV). The influence of middle-energy Ar^+ bombardment on the XPS spectra of the crystal surface was also investigated in the present work because this surface treatment method is generally used in epitaxial technologies. As can be seen from Fig. 2, all peculiarities of the survey XPS spectrum, except of C (O) 1s lines, are attributed to the core-levels or Auger lines of the atoms constituting the Tl_4HgI_6 compound. The origin of the C 1s line on the survey XPS spectrum of the pristine Tl_4HgI_6 single crystal surface is explained by hydrocarbons adsorbed from air, while the O 1s line is due to adsorbed oxygen-containing species from air.

The Tl_4HgI_6 single crystal surface was bombarded with Ar^+ ions (3.0 keV, ~ 5 min, ion current density was set to be $14 \mu\text{A}/\text{cm}^2$). Fig. 3 presents the XPS Tl 4d and Hg 4d core-level spectra of the Tl_4HgI_6 single crystal surfaces, both pristine and Ar^+ ion-bombarded.

Our XPS measurements indicate that the values of binding energy of the core-level electrons of thallium and mercury atoms do not change within the accuracy of the present experiments (± 0.05 eV) in the case of the Ar^+ -bombardment of the Tl_4HgI_6 single crystal surface (Fig. 3); however the XPS results indicate partial sensitivity of the surface with respect to the Ar^+ ion-bombardment. Our XPS measurements indicate that the Ar^+ -bombardment causes non-stoichiometry of the topmost layers. In particular, after the Ar^+ ion-bombardment of the Tl_4HgI_6 surface, the Hg content in the top surface layers of the Tl_4HgI_6 single crystal decreases by about 29%. This fact allows for concluding that in the Tl_4HgI_6 compound the chemical Hg–I bonds are significantly weaker as compared with the Tl–I bonds. The similar effect of decreasing the Hg content was detected previously for a series of mercury-containing halides, in particular Tl_4HgBr_6 [6], $\text{Tl}_{10}\text{Hg}_3\text{Cl}_{16}$ [7] and Cs_2HgX_4

(X=Cl, Br, I) [8-10]. Furthermore, our XPS measurements indicate that the breaking Hg–I bonds in the topmost surface layers due to the Ar⁺ ion-bombardment of the Tl₄HgI₆ single crystal causes the binding energies of the XPS I 4d core-level electrons to increase by about 0.15 eV. Therefore, negative charge of I atoms in the topmost surface layers of the Tl₄HgI₆ crystal decreases due to the breaking Hg–I bonds caused by the Ar⁺ ion-bombardment. Nevertheless, the above surface treatment of the Tl₄HgI₆ single crystal does not change significantly the energy distribution of the electronic states within the valence band region. Therefore, partial densities of the electronic states of Hg atoms into the valence band of the Tl₄HgI₆ compound are smaller as compared with partial densities of the electronic states associated with Tl and I atoms.

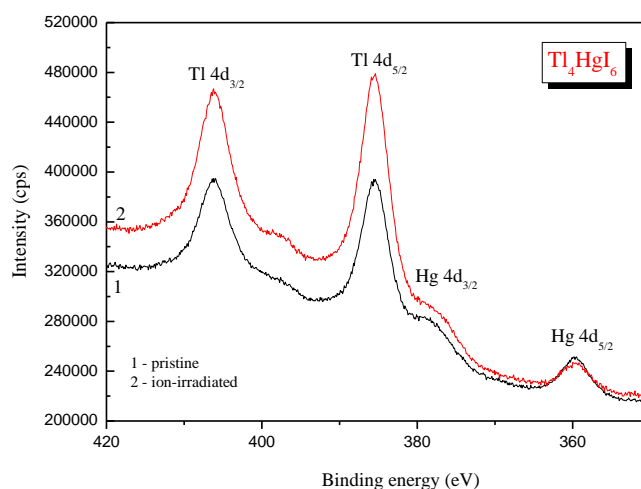


Fig. 3. XPS Tl 4d and Hg 4d core-level spectra recorded for (1) pristine and (2) Ar⁺ ion-bombarded surfaces of the Tl₄HgI₆ single crystal

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