Resonant photoemission studies of Gd/PbGdTe

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Abstract. The paper presents the experimental results of the electronic band structure study of the clean PbGdTe surface and this surface additionally doped with gadolinium atoms. Gadolinium thin films (0.4 and 1 nm) were grown epitaxially on the PbGdTe substrate. After the second evaporation the sample was annealed. Heating of the sample covered by metal atoms led to the diffusion of the gadolinium atoms into the surface layer of the sample. After each stage of the sample treatment (surface cleaning, Gd evaporation and annealing) resonant photoemission spectra were acquired for the photon energy range of 130-152 eV, corresponding to the Fano-type Gd 4d-4f resonance. The emission from the Gd 4f shell of the atoms built into the surface layer of PbGdTe was revealed and its binding energy was determined as equal to 10.4 eV

Keywords: resonant photoemission, gadolinium, synchrotron radiation

Introduction

PbTe - a narrow-gap semiconductor - attracts considerable interest due to its application as a material for thermoelectric devices, infrared detectors and lasers in the range 3-30 µm [1]. Gadolinium-doped PbTe becomes a diluted magnetic semiconductor crystallizing in the rock-salt structure. Gadolinium, as a metal, is a prototype Heisenberg ferromagnet in which the magnetic moments of atomic-like 4f states are coupled via the exchange interaction with the conduction electrons (the RKKY mechanism [2]). In IV-VI – based diluted magnetic semiconductors, the Gd 4f and Gd 5d levels play particularly important role in the interactions between gadolinium ions. Such coupling proceeds via d-f intra-ion and d-d inter-ion interactions and it depends on population of the Gd 5d orbital (related to the Fermi level position). The binding energies of 4f and 5d electrons are crucial parameters for description of this mechanism.

We present results of the resonant photoemission study of the electronic structure of Gd/PbGdTe prepared in situ (under ultra high vacuum conditions) by deposition of Gd on the PbGdTe surface. The Gd-related features do not manifest itself in the spectra of epitaxial layers of PbGdTe, due to low Gd contents (1.8%). In order to reveal and identify such features, we undertook an attempt to increase the Gd content in the subsurface layer of the samples by deposition of the metal on the sample surface and annealing the system.

Resonant photoemission spectroscopy was applied in order to follow the changes in the surface composition and its electronic structure. This technique is based on the Fano-type Gd 4d-4f resonance which leads to strong increase of emission from Gd 4f shell and helps to reveal structures derived from Gd 4f states. For the system containing Gd ions we consider the following processes:

\[ \text{Gd}^{10}4f^7 + h\nu \rightarrow \text{Gd}^{10}4f^6 + e^- - \text{common photoemission}, \]
\[ \text{Gd}^{10}4f^7 + h\nu \rightarrow [\text{Gd}^{10}4f^6]* \rightarrow \text{Gd}^{10}4f^6 + e^- - \text{intra-ion excitation followed by autoionization}, \]

where * denotes an excited state and e^- - emitted photoelectron.

The quantum interference between these processes manifests itself in a Fano-type resonant enhancement of the partial photoemission yield as well as of radiation absorption. The photoemission intensity in the resonance region is described by the Fano line shape, which includes maximum and minimum called a resonance and an antiresonance, respectively.

Since the photon energy has to be tuned to the energy of the intra-ion excitation, use of synchrotron radiation source with intense, continuous spectrum in the soft x-ray range was indispensable.

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Experimental conditions
The PbGdTe layers were grown by an MBE method (with use of PbTe, Te, and Gd solid sources) in the Institute of Physics of the Polish Academy of Sciences (Warsaw, Poland). A BaF$_2$ monocrystal, freshly cleaved along the (111) plane, was used as a substrate with good lattice parameter matching. Before the growth process the substrate was preheated at the temperature of about 500°C. Subsequently, a 0.6 μm thick PbTe buffer layer and a PbGdTe layer were deposited at the temperature of about 270°C. Composition of PbGdTe was analyzed by means of the energy dispersive x-ray fluorescence which revealed Gd content of 1.8 at.%. For photoemission experiments, surfaces of PbGdTe were cleaned by sputtering with Ar$^+$ ions and annealing about 6 hours at the temperature of 325°C. Gadolinium atoms were evaporated on the clean PbGdTe layer from an effusion cell. They were deposited stepwise with the layer thickness of 0.4 and 1 nm. After second deposition stage the Gd/PbGdTe system was annealed at the temperature of 320°C for 3.5 hours.

The photoemission measurements were performed and photoelectron energy distribution curves were collected in the regime of resonant photoemission after each stage of the system preparation procedure. The reported photoemission measurements were performed at the FLIPPER II system in HASYLAB (Germany). Synchrotron radiation was used in the photon energy range 130-152 eV. The energy scale of the spectra presented in this paper was set with respect to the Fermi level position (as measured for a reference metallic sample). The overall energy resolution was kept at 250 meV.

Results and discussion
The resonant photoemission spectra were measured for the clean surface of PbGdTe sample, after subsequent stages of Gd evaporation (for Gd layer thickness of 0.4 and 1 nm) and after annealing. The valence band of the clean PbGdTe layer (0 - 13 eV) has the main maximum at 4.8 eV and three weaker features at 2.3, 8.3, and 11.3 eV (Fig. 1). According to the photoemission studies of PbTe [3,4] and theoretical calculations of its band structure [5], the features at about 2.3 eV correspond to Pb 6p and Te 5p states. Those at 8.3 and 11.3 eV correspond to emission from bands of Pb 6s and Te 5s, respectively. The main maximum of the PbGdTe valence band (at 4.8 eV) does not correspond to any feature reported for pure PbTe. In order to reveal Gd 4f-related contribution to PbGdTe electronic structure, a set of photoemission spectra was acquired for energies close to Gd 4d-4f resonance. However, some increase of the maxima at 8.3 and 11.3 eV for photon energies 150-152 eV does not indicate conclusively presence of Gd 4f contribution in this part of the band structure of the system. The maxima related to core levels of the sample constituents appear at the binding energies of 19.3 eV and 21.8 eV (spin-orbit split Pb 5d$_{5/2}$ and Pb 5d$_{3/2}$ levels) as well as at 40.4 eV and 41.7 eV (Te 4d$_{5/2}$ and Te 4d$_{3/2}$ with a satellite structure at about 50 eV). The energy positions of Pb 5d and Te 4d are consistent with those observed for bulk PbGdTe [6].

The deposition of gadolinium atoms on the PbGdTe surface led to appearance of strong Gd-related features and helped us to reveal them in the spectra of Gd/PbGdTe system. Fig. 1 shows the set of the valence band spectra of Gd/PbGdTe covered with 1 nm thick layer of Gd and annealed at 325°C, obtained for photon energy range 130-150 eV. The intensity of the main feature (10-12 eV) strongly depends on the photon energy and changes in accordance with Gd 4d-4f resonance. Therefore we interpret it as the emission from Gd 4f. This feature consists of two components with maxima at 10.7 and 11.6 eV.

Figure 1. The photoemission spectra of PbGdTe covered with 1 nm thick Gd layer after annealing (at 320°C for 3.5 hours) near the Gd4d \rightarrow Gd 4f excitation.
An analysis of relative intensities of these components at subsequent stages of Gd/PbGdTe system formation enabled us to discuss their origin.

Fig. 2 shows the spectra of Gd 4f obtained for the resonance photon energy (150 eV) from the PbGdTe surface after evaporation of 0.4 nm and 1 nm of Gd and after annealing. The curves were normalized to the total area of the Gd 4f peak scaled by the amount of deposited gadolinium. For 0.4 nm of Gd deposited on the surface, a single maximum appears at 10.7 eV (Fig. 2b). Its binding energy is markedly higher that that of metallic Gd (8.7 eV [7], 8.05 for bulk atoms, 8.45 for surface atoms [8]). The binding energies of the Gd 4f peak in oxidized gadolinium (9.05 eV [8]) and other metallic systems (Gd on W - 8.8 eV [9], GdCu – 8.4 eV [10] and Gd on Cu - 8.6 eV [11]) were also lower than 10.7 eV. In bulk PbGdTe, the Gd 4f binding energy (measured with respect to the valence band edge as the position of the J=0 component) was equal to 9.57 eV [12]. The position of the majority cation core level (Pb 5d<sub>5/2</sub>) was 18.8 eV [12]. So, the difference of about 0.5 eV in the position of the peaks can be ascribed to a difference in the work function of the samples. As a consequence, the energy position of the Gd 4f maximum (much closer to the position of Gd 4f in bulk PbGdTe than in metallic Gd) justifies assumption that gadolinium atoms, deposited on the surface of PbGdTe, interact with it and enters into the surface layer of the sample. Since the shape of this Gd 4f derived contribution corresponds to the calculated spectrum with 4f<sup>6</sup> final-state multiplet splitting [13], we compared our experimental results with the shapes of calculated Gd 4f<sup>7</sup>→4f<sup>6</sup> photoemission spectra. The calculated multiplet lines were convoluted with a Gauss lineshape to imitate the broadening of the measured spectra. This procedure gave us the energy position of the J=0 component (a measure of the Gd 4f binding energy) equal to 10.4 eV.

Further deposition of Gd leads to an appearance of the second component of the Gd 4f maximum (at 11.6 eV), stronger than that at 10.7 eV (Fig. 2c). Annealing of the sample induces an increase of the first component (10.7 eV) and the intensities of both components become approximately equal (Fig. 2d). Since the energy position of the second feature does not correspond to that of metallic Gd, the related Gd atoms must also form some species resulting from interaction with the substrate. Annealing of the system at 325°C causes change in the binding of Gd on the surface. The similar shape of both

![Figure 2](image)

**Figure 2.** Photoemission spectra for Gd 4f measured at 150 eV a) clean sample b) after first Gd evaporation c) after second Gd evaporation d) after annealing of the PbGdTe/Gd.

![Figure 3](image)

**Figure 3.** Gd 4f contribution to the Gd/PbGdTe photoemission spectra (dots) shown together with a profile of emission from an f<sup>7</sup> shell (line) and bars indicating positions of the multiplet components.
Gd 4f components shows that all Gd atoms have the 4f shell occupied by seven electrons. However, transition from Gd$^{2+}$ to Gd$^{3+}$ corresponds to the ionization of the electron from 5d shell. It was estimated for SnGdTe that this process can lead to the increase of the binding energy of 4f electrons by about 0.1 eV [14]. So, this does not account for the observed 0.9 eV difference between the Gd 4f peak components. Further information about possible Gd$^{2+}$ to Gd$^{3+}$ transition can be extracted from the analysis of the edge of the valence band. The feature which can be related to Gd 5d appears as a shoulder on the edge of the valence band after the first stage of Gd deposition. Then, it transforms into a maximum at 3.3 eV for the thicker Gd layer. Annealing reduces the intensity of this part of the spectrum. It becomes similar to that observed after the first Gd deposition but the shoulder at 3.3 eV is reduced much more. If we assume that this feature corresponds to the Gd 5d level, its decrease due to annealing may result from ionization of this level in the atoms built into the PbGdTe crystal. This would lead to an increase of the Gd 4f binding energy after annealing, in contrast with the observed 0.9 eV decrease of this energy. So, the observed net energy separation between two components of the Gd 4f feature must result from other differences in chemical and/or structural state of the deposited gadolinium. Two possible interpretations can be considered. Firstly, the surface related components of cation core levels in semiconductors have higher binding energies with respect to the bulk component. Secondly, Gd 4f emission from gadolinium clusters manifest itself as a complex feature at 9-12 eV [15]. Final interpretation of the Gd 4f component at 11.6 eV needs further studies by other experimental techniques.

Summary

The MBE grown PbGdTe layers covered in situ with Gd were investigated by resonant photoemission at the Fano-type Gd 4d-4f resonance. Sets of photoemission spectra were acquired for the clean surface of PbGdTe sample, after subsequent stages of Gd evaporation (for the layer thickness of 0.4 and 1 nm) and after annealing of such structure (at 325°C for 3.5 hours). Analysis of the collected photoemission spectra made it possible to reveal two Gd 4f - related features in the emission from Gd/PbGdTe. One of them has been ascribed to the emission from Gd atoms built into the substrate, the other – to Gd forming some other phase distributed on the surface. The binding energy of Gd 4f shell of the atoms built into the surface layer of PbGdTe has been determined as equal to 10.4 eV.

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