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Photoemission study of (PbEuGd)Te layers under Gd or Te atoms treatment

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Abstract

Substitution of Gd^{3+} for Eu^{2+} ions in EuTe leads to the introduction of Gd 5d electrons to the conduction band and antiferromagnetic order of EuTe (Heisenberg magnetic semiconductor) can be replaced by ferromagnetic state due to RKKY interaction. The layers were grown by MBE method on BaF_2 (1 1 1) substrate. Layer of Te deposited on top of (EuGd)Te protects surface of oxidation. Heating in 320 °C leads to Te atoms desorption and to improvement of the layer electronic structure. Additional Gd atoms were sequentially deposited on the layer of (PbGd)Te and set of Fano resonance curves were observed for ions of Gd. The Fano type photoemission resonance corresponding to the 4d–4f transitions were studied for Eu and Gd.
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1. Introduction

The rare earth metal atoms chalcogenides like EuTe belong to the family of ionic Heisenberg magnetic semiconductors [1]. The EuTe doping by Gd leads to substitution of Gd^{3+} ions for Eu^{2+} ions. As result the electrons of Gd 5d are introduced as conducting electrons in these compounds [2]. In this case, interaction via free electrons (RKKY) in particular conditions can destroy the antiferromagnetic order observed in insulating layers of EuTe and replace it by ferromagnetic state in n-type (EuGd)Te layer. The component materials are well lattice matched, rock salt structure with $a = 6.59$ Å and 6.46 Å for (EuGd)Te and PbTe relatively. The possibility to obtain different kind of nanostructures of these materials is expected to be useful for e.g. growing of spin polarized injector of charge carriers into semiconductor [3–5].

The paper presents results of resonant photoemission [6,7] study of the electronic structure of MBE grown layer of (EuGd)Te protected by Te layer and layer of (PbGd)Te covered by Gd atoms and annealed in situ.

1.1. Sample preparation and experimental conditions

The layers were grown in MBE machine using effusion cells for Pb, Eu, Gd and Te. The crystal of BaF_2 (1 1 1) surface (rock salt structure, lattice constant $a_0 = 6.20$ Å) freshly cleaved in air and annealed in 560 °C in UHV preparation chamber was used as substrate for deposition. The buffer layer of EuTe of about 50 nm thick was deposited at substrate temperature 270 °C. The layers were deposited on top of buffer layer at substrate temperature 270 °C. The protective layer of Te with thickness of about 100 nm was deposited on top of prepared (EuGd)Te (rock salt structure, lattice constant $a_0 = 6.59$ Å, gadolinium content 1 at.%,) ternary alloy layer. One of the investigation goals was to determine the acceptable thermal annealing conditions for EuGdTe protected by Te layer. After every annealing process the photoemission spectra were measured to compare influence of annealing on height and sharpness of the peaks.

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The photoemission data were obtained with the Tunable Photoelectron Spectrometer with Flipper II monochromator in beam line E1 of synchrotron storage ring at HASYLAB synchrotron radiation laboratory. Angle-integrated photoemission spectra were recorded using a cylindrical-mirror energy analyzer. The overall energy resolution was typically 250 meV. All spectra were normalized to the photon flux and secondary electron background has been subtracted. The binding energy scale was referred to the Fermi level of a thick tantalum plate. The spectra were taken for the monochromatic radiation chosen in photon energy range between 100 eV and 160 eV. The spectra were recorded in the region from the valence band edge to the energy 50 eV (including Te 4d core level).

The facilities of this experimental station permits to obtain the clean surface in situ under UHV by Ar ions bombardment and annealing the sample in the preparation chamber as well as permits sequential deposition of Gd atoms. The base pressure in the analyzer chamber was 5×10^{-10} mbar.

2. Results and discussion

For the layer of (EuGd)Te protected by Te layer it was important to determine proper temperature (creation of new tellurides) and time of annealing in UHV to avoid decomposition on the sample surface (lack of tellurium). Fig. 1 presents the set of EDCs corresponding to the sequential sample treatments, indicated for each curve. The sample was not heated over 320 °C. On the lowest curve (3 h, 240 °C) the sufficient contribution of electrons 4f of both Eu^{2+} and Eu^{3+} and Te 4d peak is not sharp and spin–orbital splitting of it is not evident. The remarkable effect was observed after annealing at $T = 320$ °C during 21 h and then for 20 h. The concentration ratio Eu^{3+}/Eu^{2+} becomes negligible small and Eu^{2+} peak became sharp and narrow. Furthermore, the Te 4d peak becomes also narrower than before and its spin–orbital splitting is distinctly visible. Procedure of annealing leads to the preparation of clean surface and to remarkable improvement of the measured electronic structure caused due to improvement of the crystalline structure and stoichiometry of (EuGd)Te layer.

Set of the spectra: valence band, Eu 4f, 5p and Te 4d core levels of (EuGd)Te layer is presented in Fig. 2. The spectra were taken for set of radiation energies $h\nu$ in region 120–153 eV of possible Fano resonances 4d–4f corresponding to Eu^{2+} and Eu^{3+} ($h\nu = 141$ eV and 145 eV respectively). Sharp peak located at the valence band edge (vbe) is attributed to the 4f multiplets of ion Eu^{2+}. A weak broad structure with maximum at 7.5 eV can be attributed to the Eu^{3+} 4f multiplet. The value of the resonance energy Eu 4d → 4f transition for 2+ ions of europium in our samples is at about 141 eV and antiresonance energy at 132 eV while for 3+ ions it is at about 145 eV and 139 eV relatively [8–11]. The spectra well correspond to DOS calculation of EuTe by augmented-plane-wave (APW) method [12,13], in which Eu^{2+} 4f states were found at top of the occupied electronic states and they are located at the edge (Γ_{15}) of the valence band. Low concentration of Gd (0.03 at.%) avoid observation of Gd electrons [14]. Proper annealing of (EuGd)Te/Te

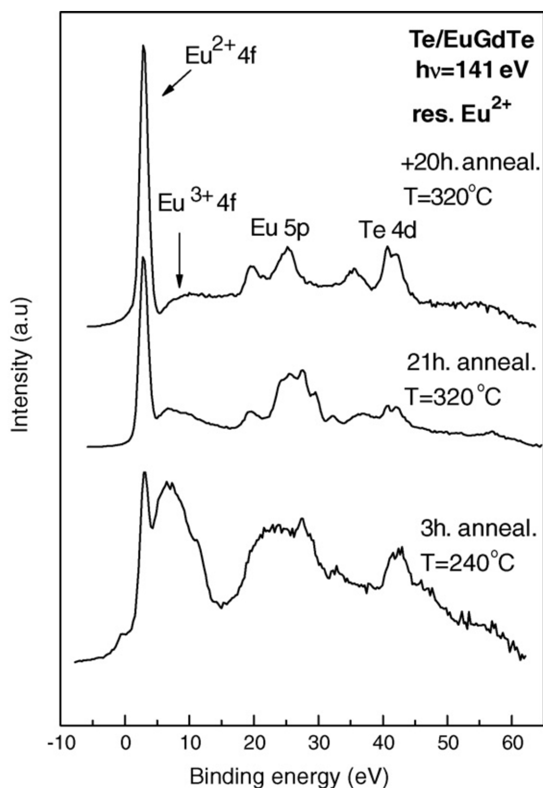

Fig. 1. Set of photoemission spectra of Te/(EuGd)Te after annealing in situ in UHV. Spectra contain valence band, Eu 4f, 5p and Te 4d core levels measured after indicated treatment.

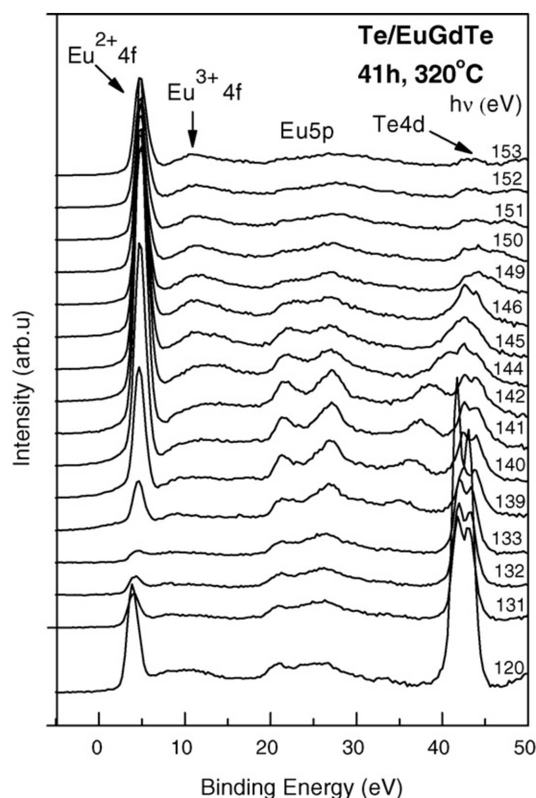

Fig. 2. Set of photoemission spectra measured in the $h\nu$ energy region 120–152 eV corresponding to Fano resonance region of Eu 4d–4f transition.

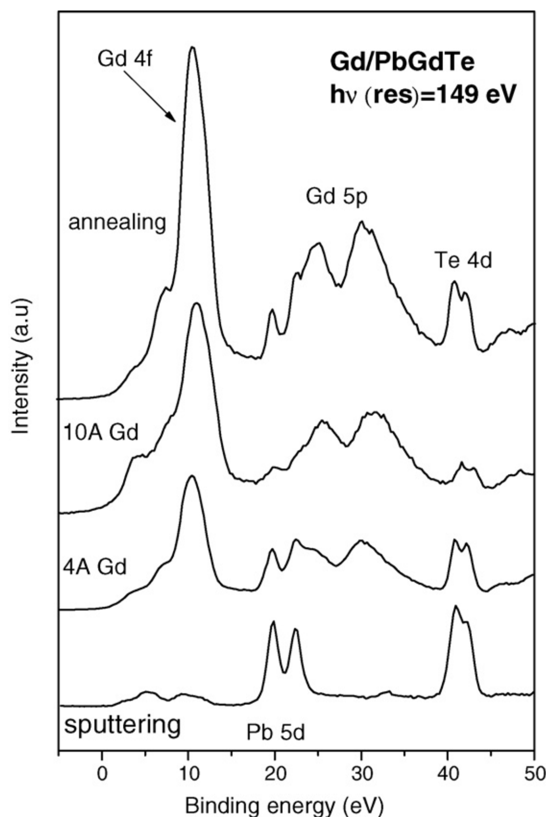

Fig. 3. Set of photoemission spectra of (EuGd)Te layer under deposition of Gd atoms and annealing.

layer aloud to form crystalline clean surface with negligible Eu^{3+}/Eu^{2+} ions concentration ratio (important for practical aspects).

The resonant photoemission study of Gd 4f, 5p and 5d electrons contribution was performed for (PbGd)Te layer with Gd atoms deposited on it. Clean surface of the layer was obtained by argon ion etching and annealing. Gadolinium thin film was deposited on (PbGd)Te (see Fig. 3) with sequential deposition of thickness 4 and then 10 Å. Set of EDCs acquired for (PbGd)Te layer covered with 1 nm thick Gd layer is presented in Fig. 3. Dominating in the spectra is Gd 4f peak splitting on peaks located at 11 eV and 12.3 eV. Both peaks exhibit the resonant behavior but the peak at 11 eV possesses resonance energy at 145 eV while peak at 12,3 eV possesses it at energy 150 eV. This behavior of Gd 4f peak can be well correlated to the behavior of small peak appearing at 3.3 eV. This peak can be prescribed to Gd 5d electrons. On the top surface of the layer the ions Gd^{2+} and Gd^{3+} can occur and first peak of them is giving the contribution to these two peaks (Gd^{2+} 4f and Gd^{2+} 5d as a 11.0 eV and 3.3 eV) while the second one, Gd^{3+}, gives contribution only to the peak at 12.3 eV. The resonance of Gd^{2+} 5p occur parallel to the resonance of Gd^{2+} 4f. Ions Gd^{2+} excited in Fano resonance for transition Gd 4d–4f can relax by emitting Gd 5p electrons. Photoemission of electrons from Pb 5d (see Fig. 4) is strongly attenuated by Gd layer located at the top part of sample. Peak of Te 4d (40 eV) is changing with the cross section dependence on $h\nu$ energy and like Pb 5d is strongly attenuated by top Gd layer.

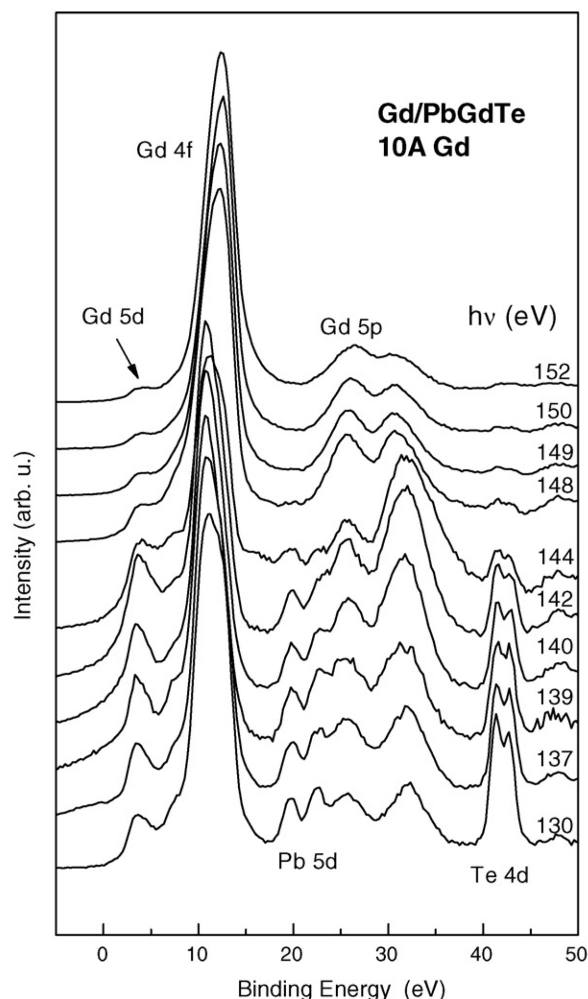

Fig. 4. Set of photoemission spectra of (EuGd)Te layer after deposition of Gd layer 1.0 nm thick.

3. Summary

Prolonged annealing of (EuGd)Te/Te layer (41 h, 320 °C) covered by protected layer of Te leads to desorption of tellurium from the surface and to formation of crystalline and clean surface of sample.

Electrons Eu^{2+} 4f multiplet was found located at vbe while for Eu^{3+} it was located at the region between 3.5 eV and 8.5 eV below it. Electrons Gd 4f were found at 10 eV below the vbe, Gd 5d at the vbe and Gd 5p at the region between 25 eV and 35 eV below the vbe. The deposited 1 nm Gd layer creates Gd^{3+} and Gd^{2+} at surface region. It can correspond to Gd^{3+} ions contributing as donor ion in (EuGd)Te and to Gd^{2+} ion creating another kind of surface defects with metallic Gd islands.

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