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Photoemission study of Eu 2+/3+ ions in ferromagnetic (Eu,Gd)Te semiconductor layers

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(Eu,Gd)Te ferromagnetic semiconductor layers grown by molecular beam epitaxy technique on BaF_2 (111) monocrystalline substrates were investigated by resonant photoemission spectroscopy using synchrotron radiation. In n-(Eu,Gd)Te layers, a ferromagnetic transition induced by electron concentration is observed. Magnetic as well as electrical properties of this material depend strongly on the charge state (2+ vs. 3+) of Eu and Gd ions known to be sensitive to crystal stoichiometry and formation of oxide complexes. The relative concentration of Eu^{2+} and Eu^{3+} ions was determined from the analysis of the resonant photoemission energy distribution curves (EDC), measured at photon energies close to 4d–4f resonance. After various in-situ annealing and Ar sputtering procedures, a clear improvement of crystal stoichiometry of (Eu,Gd)Te layers was observed as manifested by the increase of Eu^{2+} intensity in the spectra. Contribution of Eu 4f shell to the total density of states was also analyzed and found at the valence band edge for Eu^{2+} ions and about 6 eV lower for Eu^{3+} ions.

Key words: *spintronics; ferromagnetic semiconductor; rare earth compound; photoemission*

1. Introduction

Due to a strong ionic bonding in EuX (X = O, S, Se, Te), Eu ions are expected to be divalent in all members of the group of europium monochalcogenides resulting in a half-filled $4f^7$ shell of Eu. It yields spin only magnetic moment $S = 7/2$ localized on Eu ions in the rock-salt crystal lattice of EuX. This feature makes these materials an excellent example of a model Heisenberg magnet. In the EuX family, there are two ferromagnets (EuO and EuS) and one antiferromagnetic material (EuTe), whereas EuSe exhibits a more complicated phase diagram due to the compensation of ferro-

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magnetic (nearest neighbour) and antiferromagnetic (next nearest neighbour) exchange interactions [1–4]. Doping EuX with an electrically active element brings an additional indirect exchange interaction between magnetic moments of Eu via spin polarization of quasi-free carriers (the Ruderman–Kittel–Kasuya–Yosida, RKKY mechanism). EuX doped with gadolinium is particularly interesting. Gd ions substituted in (Eu,Gd)X are expected to be in 3+ charge state having the same electronic ($4f^7$) configuration. This substitution does not affect the magnetic subsystem but supplies the material with quasi-free electrons in the conduction band. Assuming that each Gd ion gives one extra electron, one can obtain very high concentration of electrons ($n \approx 1.4\times10^{20}$ cm^{-3} corresponds to 1 at. % of Gd in EuTe). For bulk (Eu,Gd)X increase of critical temperature with increasing Gd concentration and, in particular, transformation type of the magnetic transition from antiferro- to ferromagnetic in the case of (Eu,Gd)Te at Gd content about 5 at. % was reported in [1]. Hence the latter makes it possible to change simultaneously both electrical properties, from insulator for EuTe to n-type metallic conductivity for (Eu,Gd)Te, and magnetic ordering from antiferromagnetic to ferromagnetic, respectively.

Eu (as well as Gd) is known to form not only monochalcogenides (EuX) with Eu ions in 2+ charge state but also other compounds like Eu_2X_3 with Eu ions in 3+ state. Detailed experimental information on Eu charge state in (Eu,Gd)Te is very important for both magnetic and electrical properties of this material. It was reported that an excess of Te in (Eu,Gd)Te can result in a strong decrease of very high concentration of electrons, even leading to a total compensation of charge carriers and dramatic changes in magnetic properties [5]. There was also observed a behaviour qualitatively different from a typical response of ferromagnetic material on applied external magnetic field for n-(Eu,Gd)Te which can be attributed to creation of complexes other than Eu–Te or Gd–Te [6]. In this work, we use resonant photoemission spectroscopy technique to verify the Eu charge state in (Eu,Gd)Te layers grown by molecular beam epitaxy on BaF_2 (111) substrates. We analyze the influence of various annealing and sputtering procedures on the Eu^{2+}/Eu^{3+} concentration ratio. We also determine the binding energy of Eu ion states derived from magnetic 4f orbitals with respect to valence band edge of (Eu,Gd)Te. This experiment is based on the Fano effect when the energy of excitation photons is adjusted to 4d–4f transition which is manifested in an asymmetrical shape of photoemission spectra observed as maximum and minimum at the energies corresponding to resonance and anti-resonance [7].

2. Experimental results

The (Eu,Gd)Te epitaxial layers were grown using a home-built MBE system equipped with effusion cells for Eu, Gd and Te solid sources. Freshly cleaved, (111)-oriented BaF_2 monocrystals were used as substrates. First, an EuTe buffer layer, up to 0.1 μm thick, was grown, and next, 0.25 μm thick (Eu,Gd)Te layer was deposited. The substrate temperature during the growth of both layers was about 270 ºC. *In-situ* growth control using reflection high-energy electron diffraction (RHEED) revealed well defined streaky pattern indicating a two-dimensional mode of layer growth. Intensity oscillations of the RHEED specular spot allowed us to determine quite low rate of growth of 0.1 ML/s (ML – monolayer). X-ray diffraction (XRD) measurements proved good monocrystallinity of the epilayers with full width at half maximum (FWHM) X-ray rocking-curve parameter in the range of 200–400 arcsec. From energy dispersive X-ray fluorescence (EDXRF) analysis, the Gd content was determined to be typically close to 1 at. %.

The photoemission experiments were performed at the FLIPPER II beam line at the HASYLAB synchrotron radiation laboratory in Hamburg. Angle-integrated photoemission spectra were recorded using a cylindrical-mirror energy analyzer (CMA -type, PHI 25-260) with energy resolution of 250 meV. (Eu,Gd)Te was exposed to a beam of photons with energy in the range from 120 eV to 160 eV. The experiment was carried out sequentially. Four annealing processes (each for 3 h) were performed at the following temperatures: 240 °C, 270 °C, 300 °C and 350 °C. After each annealing process, the set of energy distribution curves (EDC) was taken. Finally, sputtering with Ar ions with an energy of 600 eV was applied for 1 h to remove the thin top layer, which may contain excess Te diffused during the annealing processes.

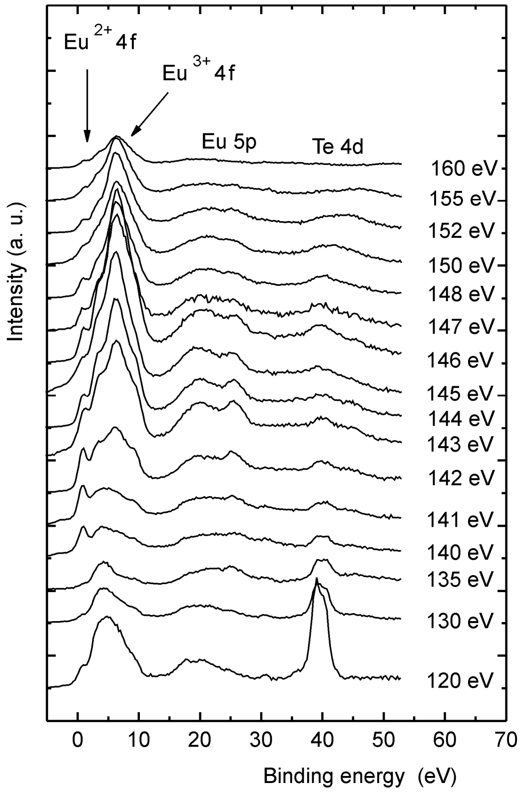

Fig. 1. The set of energy distribution curves for (Eu,Gd)Te epilayer taken after annealing of as introduced sample at 240 °C. The energy of excitation of photons equal to 141 eV corresponds to the resonance for Eu^{2+} ions. Energy position of Eu^{2+} was found to be at the edge of the valence band, while Eu^{3+} is located at approximately 6 eV below it. The spectra show major contribution of Eu^{3+} connected to an excess of Te as well as oxidation in the sample volume

Figure 1 presents a set of the energy distribution curves of photoemission spectra collected after the first annealing process at 240 °C. The graph shows peaks originated from the 4f-shell of Eu in both charge states 2+ and 3+ located at the edge of the valence band and about 6 eV below it, respectively. The 5p shell of Eu was established to be at binding energy position of about 20 eV. The Te 4d core shell with binding energy about 40 eV was also observed. In the set of EDCs, there was observed both a strong enhancement and extinction of intensity at energy position of Eu^{2+} and Eu^{3+} related to intra-ion transitions in Eu known as Fano resonance. Namely, apart from classical photoemission process (direct excitation of electron from $4f^7$ shell to vacuum) there was also observed an additional emission process as follows:

$$[\mathrm{Xe}]\,4d^{10}4f^{7} + h\nu \rightarrow ([\mathrm{Xe}]\,4d^{9}4f^{8})^{*} = [\mathrm{Xe}]\,4d^{10}4f^{6} + e \qquad (1)$$

$$[\mathrm{Xe}]\,4d^{10}4f^{6} + h\nu \rightarrow ([\mathrm{Xe}]\,4d^{9}4f^{7})^{*} = [\mathrm{Xe}]\,4d^{10}4f^{5} + e \qquad (2)$$

where * denotes excited state. Based on these results, the Fano profile shown in Fig. 2 was obtained. The resonant energies were found to be equal 141.5 and 145.2 eV for Eu^{2+} and Eu^{3+}, respectively.

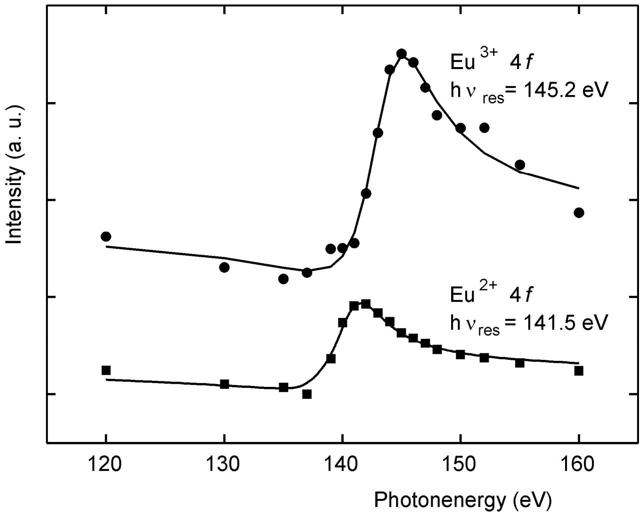

Fig. 2. Fano resonance for Eu^{2+} and Eu^{3+} ions of (Eu,Gd)Te layers obtained based on the EDC spectra measured after the first annealing process. Resonant (4d–4f transition) energies for Eu^{2+} and Eu^{3+} are marked in the figure

To verify the influence of thermal treatment on (Eu,Gd)Te epilayers, the EDC spectra at resonant energy of 141 eV were taken at sequential stages of preparation. To enhance the changes, the plots were normalized to intensity at energy position of Eu^{3+}. At the first step, for the as introduced layer, it was observed that the contribution of Eu^{3+} ions is comparable to Eu^{2+} ions. This fact can result from the excess of Te in the layer, but more likely it is related to surface oxidation. Further annealing processes show the increase of the Eu^{2+} peak intensity against the Eu^{3+} one. Despite an improvement of the stoichiometry in the sample volume due to diffusion of Te, a substantial increase of Te in thin film close to the surface was expected. This supposition was confirmed by observation of a high intensity peak originated from Eu^{3+}. To check this assumption, sputtering with Ar ions was carried out and the top layer of about 50–100 nm was removed. As shown in Fig. 3, this procedure results in a further increase of the Eu^{2+}/Eu^{3+} ratio of photoemission intensities revealing considerable decrease of Eu^{3+} ions concentration (although still observed). It seems that this is connected to the creation of oxides (Eu_2O_3). Very recent secondary ions mass spectrometry (SIMS) investigations performed on a (Eu,Gd)Te sample grown two years ago showed the incorporation of oxygen in the whole volume of the sample on a significant level. Such results point out the necessity of protecting the surface of (Eu,Gd)Te layer with Te or PbTe thin capping layer.

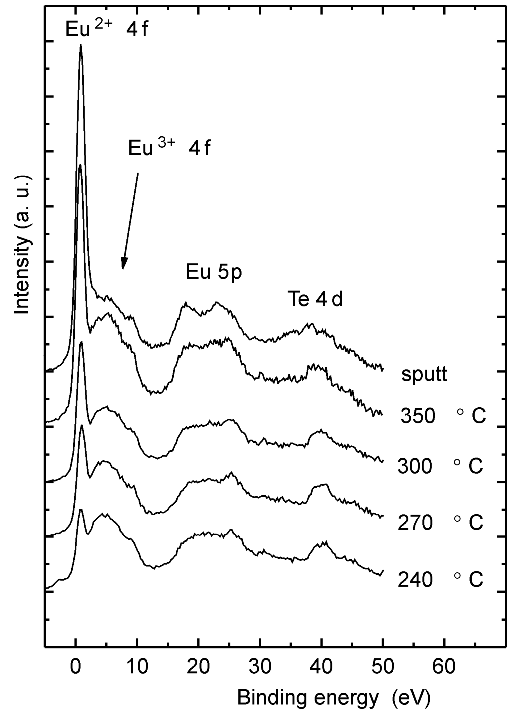

Fig. 3. EDC spectra of (Eu,Gd)Te layer after sequential surface preparation procedures (see the experimental section). All presented curves were normalized to their intensities at energy position of Eu^{3+}

3. Conclusions

In this work, the (Eu,Gd)Te epitaxial layers were investigated by resonant photoemission spectroscopy using synchrotron radiation. From the analysis of the energy distribution curves, Fano resonances were determined for both Eu^{2+} and Eu^{3+} ions at the energies of 141.5 and 145.2 eV, respectively. Contribution of Eu 4f-shell to the total density of states was found to be located at the valence band edge for Eu^{2+} ions while it was about 6 eV lower for Eu^{3+}ions. From EDC spectra measured after different annealing procedures (varying the annealing temperature) at a photon energy close to 4d–4f resonance transition for Eu in 2+ charge state, we found the improvement of crystal stoichiometry of (Eu,Gd) Te layers manifested by the increase of Eu^{2+} intensity in the photoemission spectra. The complete disappearance of Eu^{3+} contribution to the photoemission spectra could not be achieved, what we attribute to the formation of Eu oxide complexes in the layer.

Acknowledgements

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