Valence of Eu and Gd in Eu$_{1-x}$Gd$_x$Te Layers

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The Europium chalcogenides EuX (X= O, S, Se, Te) crystals belong to the family of ionic Heisenberg magnetic semiconductors, which electrical, magnetic and magneto-optical properties are determined by an interaction of the half-filled 4f-shell electrons with the valence band electrons. The substitution of Gd$^{3+}$ for Eu$^{2+}$ ions introduces conducting electrons in these compounds and qualitatively changes magnetic properties of these semiconductor alloys: in particular the antiferromagnetic order observed in insulating layers of EuTe is replaced by ferromagnetic (RKKY interaction driven) state in n-type (Eu,Gd)Te [1].

The photoemission data were obtained with the Tunable High-Energy X-ray Photoelectron Spectrometer at the X-ray wiggl er beam line BW2 of synchrotron storage ring at HASYLAB (Hamburg, Germany). An excitation energy was chosen 3000 eV to avoid overlapping of any Auger electron emission with Eu and Gd levels spectra. The angle dependent data were obtained by rotating the sample relative to the incoming beam and to the electron analyzer. Comparison of the spectra recorded at normal emission and grazing emission angle allows to distinguish surface and volume atoms contribution to the measured spectra. The spectra correspond to the valence 3+ and 2+ of Eu and 3+ of Gd ions [2].

The layers of thickness of one micron were grown by MBE method on substrate of BaF$_2$ (111) surface with EuTe buffer layer of 50nm [1]. The (Eu,Gd)Te layers were grown in the Institute of Physics PAS in Warsaw by molecular beam epitaxy on BaF$_2$ (111) substrate with EuTe buffer layer. The Eu, Te$_2$ and Gd were evaporated from separate effusion cells. The content of Gd (about 1% in measured layer) was defined by X-ray fluorescence analysis. The depositions were performed for materials with good lattice parameter matching.

The components of (Eu,Gd)Te layer are very sensitive on oxidation. The oxidation changes metallic n-type conductivity of the layer on insulating material. The oxidation of rare earth metals leads to the change of its valence. The change of the ion valence can be indicated by the change of binding energy of the core levels.

The main core level photoemission spectra of Eu, Gd, Te, O as well as valence band spectra were measured before and after sequential Ar ion etching. For surface of the sample exposed to the air, the oxidation of the surface takes place and measured Eu spectra showed the dominant Eu$^{3+}$ contribution as in Eu$_2$O$_3$ oxide. In the same time the Te core level spectra show that Te atoms on the surface are oxidized. Surface sputtering by Ar ions removes the oxidized top part of the layer and reveals the photoemission spectra of clean (Eu,Gd)Te layer. The Eu$^{3+}$ ions dominate in the spectra and the peak of oxidized Te disappears for clean surface. The high sensitivity of the surface stoichiometry on surface treatment (Ar ion sputtering, X-ray irradiation) leads to the transformation of the dominating Eu$^{2+}$ ions to Eu$^{3+}$ at the sample surface. The contribution of Eu$^{2+}$ 4f electrons to the electronic structure of the (Eu,Gd)Te was found at the top of the valence band.
The XPS core level spectra and valence band features of (EuGd)Te well correspond to the calculated multiplet structures and DOS of europium monochalcogenides.

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**References**
