REVERSIBLE VALENCY TRANSITIONS OF EUROPIUM IN MBE GROWN Eu-Mn THIN FILMS

K. Balin^{1,2*}, J. Szade¹, and Z. Celinski²

¹A. Chełkowski Institute of Physics, University of Silesia, Katowice, 40–007, Poland ²Center for Magnetism and Magnetic Nanostructures, University of Colorado at Colorado Springs,

Colorado Springs, CO 80918, USA

Keywords: europium valency, reversible valency transitions, intermetallic alloys, thin films *e-mail: katarzyna.balin@us.edu.pl

The examination of formation of unknown ordered Eu-Mn compounds and the valency of europium in MBE grown thin films were the main point of our interest. We considered that such Eubased materials, in which the control of the valency of Eu would be possible, may be applied into new classes of spin-based sensor, memory or logic devices.

Europium may exist in two valency states; metallic europium is divalent, in alloys or intermetallic compounds it may be in a divalent, trivalent or intermediate-valency state. Magnetic properties of europium are directly connected to its valency state; Eu^{3+} is non-magnetic (J = 0) while the Eu^{2+} has a large pure spin moment (J = 7/2). The ability of controlling of the Eu valency and consequently switching between the non-magnetic and the magnetic states of europium led us for study the Eu-Mn system. Such ability would be highly useful nowadays when microelectronic devices are being substituted by devices which using spin properties instead of charge degrees of freedom.

We used a MBE system to grow $\sim 10 - 40$ nm thick Eu-Mn films assuming that structural effects at interfaces in a multilayer system may be helpful in formation of new phases. The films were deposited on polycrystalline Mo buffer layer grown on Si or GaAs substrates. The *in situ* XPS measurements were performed during the controlled alloying between neighboring layers and after that process. This allowed carrying out studies in several different directions. The first one was aimed at monitoring the reaction of the film constituent elements.



Figure 1: Valency transitions of europium.

It turned out (chemical shifts and relative changes in the intensity ratio) that within the examined system the elements are inter-mixing at elevated temperatures. The second one was directed to changes in the valency of europium. The changes associated to the reaction with surrounding transition metal lead to valency transition of europium $Eu^{2+} \leftrightarrow Eu^{3+}$. Europium may remain in a divalent state ($EuMn_2$) [1], may change the valency to trivalent or show intermediate valence state (Eu_2Mn_{17}). The third one was the observation of reversible valence transitions of europium which was found to be forced by heat treatment or change of the interface resulting from covering the surface of the film.

Annealing at elevated temperatures leads to increase of the intensity of the Eu^{2+} states while the reverse "cooling down" process causes opposite $Eu^{2+} \leftrightarrow Eu^{3+}$ transition. The excitation of the Eu^{2+} states tends to decrease with the temperature increase but the reversible changes even after annealing at high temperatures do not disappear.

Such behavior, taking into account published report [2], is probably an individual property of the thin layer of Eu or its oxide in some unique environment.

Due to results obtained for MBE grown EuF_3 thin films presented in ref. 3, where X-ray absorption (XAS) and resonant photoemission (RESPE) have been used for the investigations of europium valency, we attempt to solve the issue of europium valency in Eu-Mn with the use of those techniques.

Acknowledgments: This work was supported by NSF DMR 0907053.

References

- K. Balin *et al.*, "Electronic structure, crystallographic, magnetic, and transport characterization of EuMn₂ films," *Appl. Phys.* **107** (2010) 09E154.
- [2] J.A.D. Matthew et al., "Silicide formation and valence switching at the Eu-Si interface monitored by electron energy loss spectroscopy in the reflection mode," J. Phys.: Condens. Matter 4 (1992) 8489.
- [3] J. Szade, W. Burian, Z. Celiski, T. O'Keevan, M. Zangrando, F. Bondino, E. Magnano, "Resonance induced divalent Eu states in EuF₃ ultrathin layer," *Surf. Sci.* 580 (2005) 163.