

# RESONANT PHOTOEMISSION OF $4f$ ELECTRONS ON CLEAN SEMICONDUCTOR SURFACES

E. Guziewicz<sup>1\*</sup>, B.A. Orlowski<sup>1</sup>, A. Reszka<sup>1</sup>, L. Wachnicki<sup>1</sup>, S. Gieraltowska<sup>1</sup>,  
M. Godlewski<sup>1</sup>, I.A. Kowalik<sup>1</sup>, B.J. Kowalski<sup>1,2</sup> and R.L. Johnson<sup>2</sup>.

<sup>1</sup>*Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02 – 668 Warsaw, Poland.*

<sup>2</sup>*Institut für Experimentalphysik, Universität Hamburg, Luruper Chausee 149, 22761 Hamburg, Germany.*

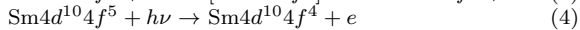
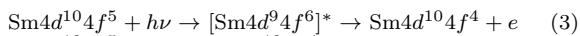
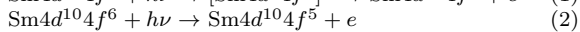
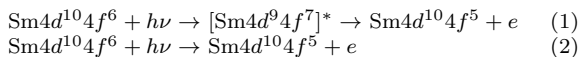
*Keywords: synchrotron radiation, samarium, zinc oxide, gallium nitride, cadmium telluride, semimagnetic semiconductors*

\* e-mail: guzel@ifpan.edu.pl

Wide band-gap semiconductors doped with rare-earth (RE) elements have experienced attention as materials for optoelectronic devices. The  $4f$  electrons of RE ions are usually highly localized and in the electronic structure of the host material and thus the  $4f^n$  electrons are only slightly perturbed compared to free ion energy levels. As a consequence, the wavelength of RE-related light emission is atomic like and almost insensitive to temperature, which usually is an attractive attribute for light-emitting devices. Because of that RE doped wide band semiconductors are attractive candidates for optoelectronic and thin film electroluminescent devices [1-3].

However, for some RE elements, for which the ionization energy of the  $4f$  shell is close to the chemical potential, a mixed-valence state occurs. This regime may arise for samarium compounds, where  $4f^6$  ( $\text{Sm}^{2+}$ ) and  $4f^5$  ( $\text{Sm}^{3+}$ ) configurations are close to the Fermi level and almost degenerate. Therefore even small changes of the chemical environment cause changes in the samarium  $4f$  configuration and thus influences the Sm valence and light emission, because  $\text{Sm}^{2+}$  and  $\text{Sm}^{3+}$  ions produce quite different photoluminescence spectra [4,5].

In the paper we present resonant photoemission results for samarium doped wide band gap semiconductor surfaces like cadmium telluride (CdTe), gallium nitride (GaN) and zinc oxide (ZnO). Samarium is a very rewarding subject for resonant photoemission (RPES) studies because its divalent and trivalent electron configurations can be characterized by distinct and well-resolved photoemission spectral features. In resonant photoemission the emission from the  $\text{Sm}4f$  shell is resonantly enhanced when photon energy is tuned to the  $\text{Sm}4d \rightarrow \text{Sm}4f$  energy threshold. For the  $\text{Sm}^{2+}$  ( $4f^6$ ) and  $\text{Sm}^{3+}$  ( $4f^5$ ) configurations, two RPES processes can be expressed as follows:



where \* denotes an excited state. Equations (1) and (2) describe resonant and classical photoemission path for  $\text{Sm}^{2+}$ , while equations (3) and (4) express these processes for a  $\text{Sm}^{3+}$  configuration.

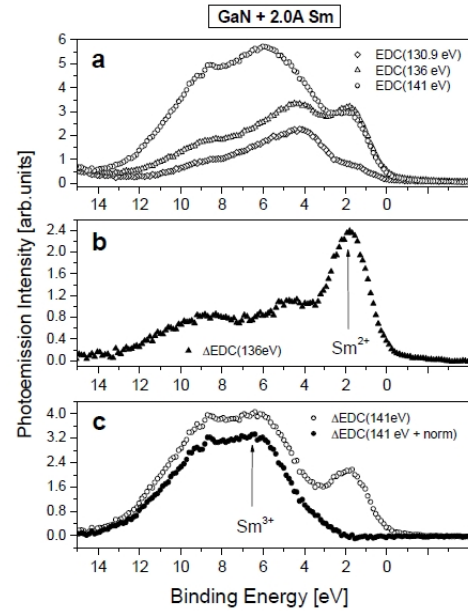


Figure 1: Valence band EDCs of the Sm/GaN system (a) taken for  $h\nu = 141$  eV, 136 eV and 130.9 eV and difference spectra  $\Delta\text{EDC}$  showing the  $4f$  contributions for  $\text{Sm}^{2+}$  (b) and  $\text{Sm}^{3+}$  (c).

In the synchrotron radiation experiments we sequentially deposited small amounts of samarium atoms on clean semiconductor surfaces (CdTe, GaN, ZnO) and via the RPES experiment we observed variations in the electronic band structure of the semiconductor systems. All experiments were performed at the Flipper II beamline in the HASY-LAB synchrotron radiation laboratory (Germany). The resonant enhancement in the photoemission intensity was observed at photon energy of 141 eV (for  $\text{Sm}^{3+}$  valence) and 136 eV (for  $\text{Sm}^{2+}$  valence), while the anti-resonance was observed at 131 eV. The difference between resonant and antiresonant photoemission spectra provides information about the  $\text{Sm}4f$  contribution to the electronic band structure of the investigated system. Valence band EDCs of the Sm/GaN system taken for  $h\nu = 141$  eV, 136 eV and 130.9 eV (a) are shown in Fig. 1 together with the difference spectra,  $\Delta\text{EDCs}$ , showing the  $4f$  contributions for  $\text{Sm}^{2+}$  (b) and  $\text{Sm}^{3+}$  (c). Analogous results for the Sm/ZnO are presented in Fig. 2.

Resonant photoemission results provide a unique possibility to observe the variation in Sm valence

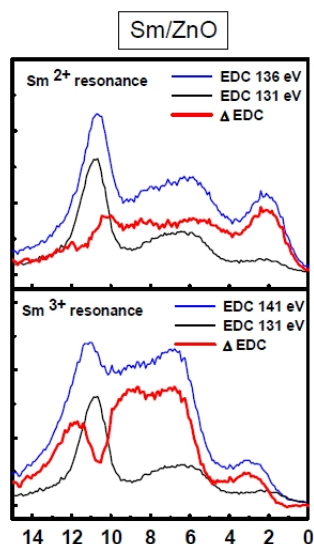


Figure 2: Valence band EDCs of the Sm/ZnO system taken for  $h\nu = 141$  eV, 136 eV and 131 eV and difference spectra  $\Delta$ EDC showing the  $4f$  contributions for  $\text{Sm}^{2+}$  (upper) and  $\text{Sm}^{3+}$  (lower). EDC spectra at the  $\text{Sm}^{2+}$  and  $\text{Sm}^{3+}$  resonance (141 eV and 136 eV, respectively).

after subsequent steps of samarium deposition onto clean semiconductor surfaces. It will be shown that samarium reacts in different ways with clean ZnO, GaN and CdTe surfaces. For CdTe and GaN the interaction of samarium with semiconductor surface is rather strong. In case of CdTe it leads to creation of Sm-CdTe compound that inhibits further diffusion of samarium atoms into the bulk [6]. In case of the Sm/GaN system [7] some Ga atoms are released and segregated. When samarium is deposited onto the clean zinc oxide surface a metallic shoulder at the Fermi level is observed even after deposition of the first Sm monolayer, but it disappears after 30 min-

utes annealing at 300°C and than the  $\text{Sm}^{3+}$  valence is strongly privileged.

It will be shown that thanks to the Resonant Photoemission experiment we can extract information on subtle changes in chemical environment of the measured semiconducting systems.

**Acknowledgments:** The research was partially supported by the European Union within the European Regional Development Fund, through grant Innovative Economy (POIG.01.01.02-00-008/08). The authors acknowledge support by MSHE of Poland research Projects DESY/68/2007 and by the European Community via the Research Infrastructure Action under the FP6 “Structuring the European Research Area” Programme (through the Integrated Infrastructure Initiative “Integrating Activity on Synchrotron and Free Electron Laser Science”) at DESY.

## Reference

- [1] S.A.M. Lima, M.R. Davolos, *Appl. Phys. Lett.* **90** (2007) 023503.
- [2] C.C. Yang, S.Y. Cheng, H.Y. Lee, S.Y. Chen, *Ceramics Int.* **32** (2006) 37.
- [3] D. Kouyate, J.-C. Ronsard-Haret, J. Kossanyi, *J. Mater. Chem.* **2** (1992) 727.
- [4] C.T.M. Ribeiro, F. Alvarez, A.R. Zanatta, *Adv. Mat.* **14** (2002) 1154.
- [5] J. Qiu, K. Miura, K. Nouti *et al.*, *Solid State Commun.* **113** (2000) 341.
- [6] E. Guziewicz, K. Szamota-Sadowska, B.J. Kowalski, B.A. Orłowski, J. Ghijsen, R.L. Johnson, *Appl. Surf. Science* **166** (2000) 231.
- [7] E. Guziewicz, B.J. Kowalski, B.A. Orłowski *et al.*, *Surf. Science* **551** (2004) 132.