Resonant photoemission study of Sm atoms on ZnO surface

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Apart from optoelectronic applications due to its intense ultraviolet near-band-edge luminescence, zinc oxide is also considered as a host material for doping with optically active impurities (such as rare-earth ions [1-2]) in view of expanding the luminescence range into the visible light spectrum. In the present work we investigate properties of ZnO doped with Sm. Samarium is a very interesting dopant for photoemission studies because its divalent and trivalent configurations are characterized by distinct and well separated photoemission features. The multiplet corresponding to the initial $4f^6$ configuration is identified within 5 eV of the Fermi level while the multiplet associated with the initial $4f^5$ configuration appears between 5 eV and 10 eV below the valence band edge. Moreover, Sm^{2+} and Sm^{3+} ions produce quite different luminescence spectra [3].

The ZnO samples were grown by atomic layer deposition (ALD) in the Institute of Physics Polish Academy of Sciences in Warsaw. The main advantage of this method is a self limitation and sequential growth process, which enables using very reactive precursors and reducing growth temperature, while keeping good crystallographic and optical parameters. The polycrystalline and epitaxial ZnO films were deposited at 300ºC on a Si and a GaN/Al_2O_3 template, respectively.

Deposition of Sm atoms onto the ZnO surface and photoemission measurements were performed at the FLIPPER II beamline in HASYLAB synchrotron radiation laboratory (Hamburg, Germany). Samarium was deposited from a Knudsen cell under ultra-high vacuum conditions at room temperature. Sm atoms were evaporated sequentially to obtain capping layers with the thickness of 1 ML, 3 ML and 7 ML. After the last deposition the samples were annealed for 0.5 and 4 hours at 300ºC. The set of energy distribution curves (EDC) was acquired after each step of the deposition and annealing processes. The investigations of Sm/ZnO system by resonant photoemission spectroscopy were carried out for the photon energy range of 130-160 eV that corresponds to the Sm4d→Sm4f Fano resonance region [4]. For the $4f^6$ (Sm^{2+}) and the $4f^5$ (Sm^{3+}) configurations, two resonant photoemission processes occur:

$$Sm4d^{10}4f^6 + h\nu \rightarrow [Sm4d^9 4f^7]^* \rightarrow Sm4d^{10}4f^5 + e \qquad (1)$$

and

$$Sm4d^{10}4f^5 + h\nu \rightarrow [Sm4d^9 4f^6]^* \rightarrow Sm4d^{10}4f^4 + e \qquad (2)$$

where []* denotes an excited state. Each of the processes described above is accompanied by the classical photoemission process as follows:

$$Sm4d^{10}4f^6 + h\nu \rightarrow Sm4d^{10}4f^5 + e \qquad (3)$$

and

$$Sm4d^{10}4f^5 + h\nu \rightarrow Sm4d^{10}4f^4 + e \qquad (4)$$

As a result of the interference between resonant and classical photoemission channels, we observe two separated resonances for divalent (channels (1) and (3)) and trivalent (channels (2) and (4)) samarium states [5]. The photoemission resonance for Sm^{3+} configuration is observed at photon energy 141 eV, whereas the resonance for Sm^{2+} configuration occurs at photon energy 136 eV [4]. Photoemission Energy Distribution Curves (EDCs) taken after each step of deposition and annealing at photon energy of both Fano resonances are shown in Fig. 1 and 2.

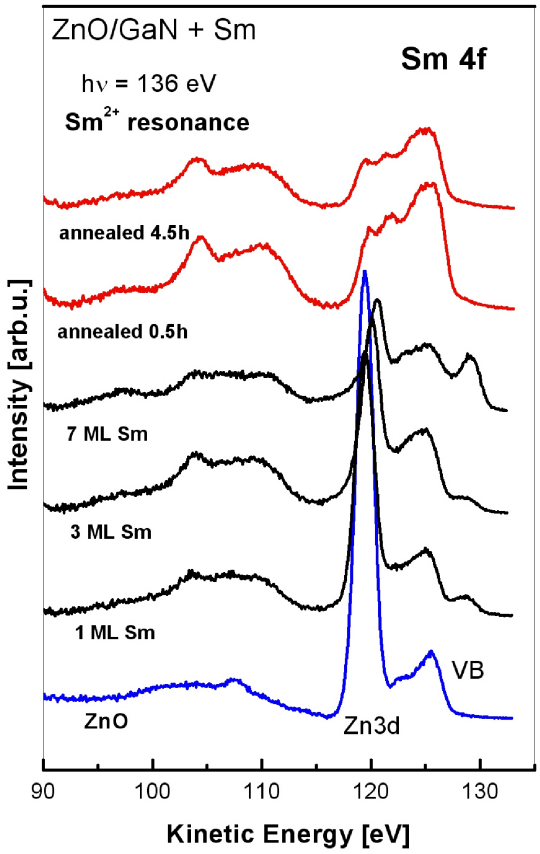

Fig. 1. *Photoemission spectra EDCs for Sm/ZnO measured at hν = 136 eV to emphasize the $4f^6$ (Sm^{2+}) emission. The spectra show the valence band and the nearest core levels.*

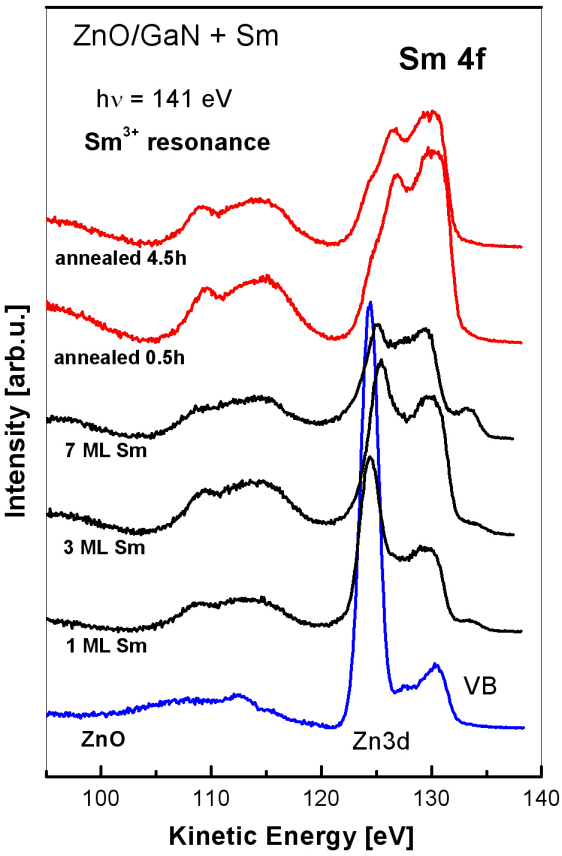

Fig. 2. *Photoemission spectra EDCs for Sm/ZnO measured at hν = 141 eV to emphasize the $4f^5$ (Sm^{3+}) emission. The spectra show the valence band and the nearest core levels.*

After each step of deposition we observed photoemission enhancement at the valence band edge, i.e. in the energy region characteristic of Sm^{2+} configuration. We also see a small increase of photoemission intensity in the energy region between 5 eV and 10 eV below the valence band edge, i.e. characteristic of Sm^{3+} configuration. After 30 min. annealing at 300ºC the peak at the valence band edge (characteristic of Sm^{2+}) disappears and the feature of Sm^{3+} markedly increases, which is the fingerprint that samarium atoms become trivalent. We also observe that the maximum of the Zn3d core level shifts to lower binding energy after samarium deposition, but returns to the previous position characteristic of ZnO crystal after 30 min. annealing. This indicates that chemical reaction between ZnO and Sm takes place at the interface region.

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