DOI 10.1007/s11182-017-0967-0

Russian Physics Journal, Vol. 59, No. 10, February, 2017 (Russian Original No. 10, October, 2016)

SECONDARY ION MASS SPECTROSCOPY OF ZINC SELENIDE CRYSTALS WITH PHOTOCONDUCTIVITY SPECTRAL MEMORY

A. V. Belenchuk,[1] N. I. Ilyinykh,[2] and L. E. Kovalev[3]

UDC 537.312.52:543.51

Keywords: zinc selenide, photoconductivity, mass spectroscopy.

Zinc selenide crystals are increasingly applied in the infrared, LED, and fiber optic technology as the detectors of X-rays and elementary particles. The analysis of ZnSe photoconductivity can facilitate identification of specific technological conditions necessary to obtain samples with preset parameters.

After preliminary optical excitation of a certain wavelength of high-resistance ZnSe, there is a splash in the relaxation curves of the photocurrent observed at irradiation with light of the other wavelengths from the region of impurity absorption. This phenomenon is a manifestation of "spectral memory" of the photoconductivity. In [1] the authors suggested a two-level model to explain spectral memory of ZnSe, and after studying the electron paramagnetic resonance spectra at optical excitation [2], these levels were related to the uncontrolled iron impurities, which were unevenly distributed throughout the whole crystal. It is known that upon the introduction into the crystal, iron tends to accumulate closely to the irregularities of the crystal structure such as dislocations and vacancies. Having an unfilled 3d-shell, the iron ions can exist in a lattice in different charge states creating corresponding levels in the forbidden zone of zinc selenide.

The influence of iron impurities on the photoelectric and luminescent properties of ZnSe was studied in many works, for instance, in [3, 4]. Secondary ion mass spectrometry analysis of the composition was mainly carried out for specially annealed bulk crystals [5] or thin films [6] of ZnSe with relatively small resistivity.

The main aim of this work was to study the composition of impurities in high-resistivity ZnSe samples possessing the phenomenon of spectral memory of the photoconductivity in order to detect traces of iron impurities by the method of secondary ion mass spectroscopy (SIMS).

The study was conducted using large-grained monocrystals of ZnSe grown from the melt under pressure without special-purpose doping by background impurities. Initial samples were obtained by cleavage and had the shape of parallelograms 10–15 mm long, 5–8 mm wide, and 2–3 mm thick. Their properties were as follows: resistivity in darkness – $\sim 10^{12}$ Om·cm; *n*-type conductivity with free electrons concentration of $\sim 10^7$ cm^{-3}; mobility in darkness ~10 cm^2/(V·s) and in light ~100 cm^2/(V·s). The X-ray diffraction analysis of ZnSe monocrystal samples indicated that all studied zinc selenide crystals had a sphalerite structure, while the coplanar faces, which were used for SIMS analysis, coincided with the (110) planes.

In order to identify the impurities in zinc selenide samples that possesses the phenomenon of spectral memory of the photoconductivity, the commercially produced secondary ion mass spectrometer MS-7201M was utilized. The primary argon ions with the energy of 5 keV and the current density on the sample surface of $(1–2)\cdot 10^{-9}$ A/m^2 were used for the ZnSe sputtering in a vacuum chamber with background pressure of $\sim 10^{-5}$ Pa.

[1]Institute of Electronic Engineering and Nanotechnology of the Academy of Sciences of Moldova, Chisinau, Moldova; [2]Ural Technical Institute of Telecommunications and Informatics Branch Siberian State University of Telecommunications and Informatics in Ekaterinburg, Ekaterinburg, Russia, e-mail: ninail@bk.ru; [3]Uman National University of Horticulture, Uman, Ukraine, e-mail: leokova60@mail.ru . Translated from Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika, No. 10, pp. 174–175, October, 2016. Original article submitted February 25, 2016; revision submitted July 7, 2016.

 1064-8887/17/5910-1718 ©2017 Springer Science+Business Media New York

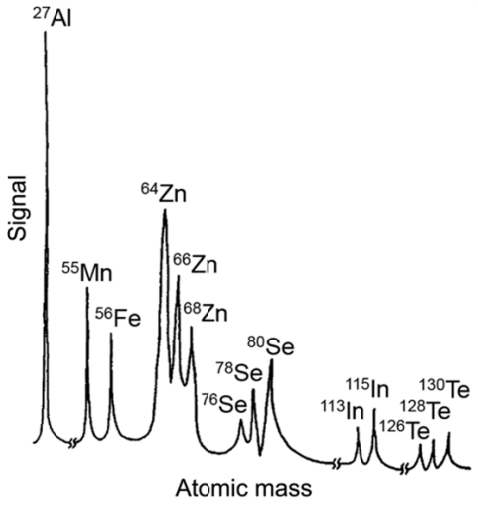


Fig. 1. Mass spectrum of high-resistance ZnSe.

During analysis of the ZnSe high-resistance samples we encountered some difficulties related to the sample surface charging by the primary ion beam. Therefore, the device was modified by the introduction of an additional electron bombardment of the sample in order to compensate the positive charge on the crystal surface. A tungsten coil was introduced near sample position as a source of the electrons. Besides, a high-purity tantalum diaphragm annealed preliminary in vacuum was placed on the sample surface to facilitate charge removing . Before using the diaphragm, the mass spectrum of tantalum foil was collected for subsequent subtraction of the Ta background peaks from the mass spectrum of ZnSe samples.

Fig. 1 shows a typical mass spectrum of high-resistance zinc selenide samples studied.

The preservation of isotope ratios in the mass spectrometer allows us to identify reliably the peaks corresponding to zinc and selenium, the main elements of the studied material. Moreover, it was possible to identify some uncontrolled impurities, such as aluminum, manganese, iron, indium, and tellurium. Reliable determination of the impurities concentrations is complicated due to the absence of relative sensitivity coefficients of the elements included in zinc selenide. According to the overall sensitivity of used SIMS device, the concentrations of the uncontrolled impurities we estimated at the level higher than $\sim 10^{17}$ cm^{-3}.

In addition, we studied the impurity composition of ZnSe samples annealed in liquid zinc and bismuth. The annealing was performed during 100 hours at 1000°C. No changes were observed in the impurity composition of the annealed samples in relation to the initial ones.

CONCLUSIONS

The proposed modification of SIMS analysis can be applied for impurities identification in high-resistance materials like not on purpose doped ZnSe monocrystals.

The SIMS analysis of impurities composition in the high-resistance zinc selenide crystals supports indirectly the hypothesis, that iron impurities, which are unevenly distributed throughout the whole crystal, are responsible for the splashes in the photocurrent relaxation curves and the phenomenon of ZnSe spectral memory of the photoconductivity.

It is shown that the annealing of ZnSe samples in liquid zinc and bismuth does not change the composition and concentration of impurities within the sensitivity range of the device ($\sim 10^{17}$ cm^{-3}). Thus, the introduction of bismuth into the crystal volume during annealing was not identified.

REFERENCES

1. L. I. Bruk, O. S. Gorya, V. A. Korotkov, *et al.* Inorgan. Mater., **31**, No. 10, 1180–1182 (1995).
2. V. A. Korotkov, L. I. Bruk, A. V. Simashkevich, *et al*., Mater. Res. Soc. Symp. Proc., **442**, 579–584 (1997).
3. Y. F. Vaksman, Y. A. Nitsuk, V. V. Yatsun, *et al*., Semicond., **45**, 9, 1129 (2011).
4. S. S. Vilchinskaya, V. I. Oleshko, and S. G. Gorina, Izv. Vyssh. Uchebn. Zaved. Fiz., **54**, No. 1/2, 138–142 (2011).
5. Ching-Hua Su, S. Feth, D. Hirschfeld, *et al*., J. Crystal Growth, **204,** Nos. 1–2, 41–51 (1999).
6. L. C. Calhoun and R. M. Park, J. Appl. Phys., **85**, No. 1, 490–497 (1999).