

# The structural defects formation in ZnS under electron irradiation with energy 400 KeV

Y Y Loginov, I V Kovalev, P V Zelenkov

Siberian State Aerospace University

31 Krasnoyarskiy Rabochiy prospect, Krasnoyarsk, 660037, Russia.

E-mail: loginov@sibsau.ru

**Abstract.** The formation of structural defects in grown from the vapour phase ZnS crystals after electron irradiation with energy of 400 keV and intensity of  $1 - 4 \cdot 10^{19} \text{ e/cm}^2 \cdot \text{s}$  in situ in electron microscope was studied. It is shown that under electron irradiation the small dislocation loops in size of 2.5 - 45 nm and a density of  $1.4 \cdot 10^{11} \text{ cm}^{-2}$ , as well as voids and fine particles of a new phase in size  $\leq 10 \text{ nm}$  are formed. These features can be identified from an analysis of moiré fringe contrast as phase of  $\text{ZnO}_2$ .

## 1. Introduction

The study of the formation of structural defects and changes in the properties of irradiated semiconductors is of interest both in terms of increasing their radiation resistance, and ability to manage the properties of materials under irradiation [1-5]. This is especially important for semiconductor compounds  $\text{A}_2\text{B}_6$ , because of their high sensitivity to radiation and insufficient study of these issues.

Zinc sulfide, belonging to the group of compounds  $\text{A}_2\text{B}_6$ , is used for the detection of charged particles. The high efficiency of radiative recombination of electrons and holes of the material makes it possible to use it as an active element of the semiconductor laser. Further, ZnS is a promising material of the power quantum optics.

The formation of structural defects in semiconductors during electron irradiation is possible in the conditions of electron irradiation with a high intensity  $\sim 10^{17} - 10^{19} \text{ e/cm}^2 \cdot \text{s}$  that is achievable, for example, in the transmission electron microscope (TEM). These intensities several orders of magnitude higher than the intensity of radiation in conventional industrial accelerators ( $\sim 10^{12} - 10^{14} \text{ e/cm}^2 \cdot \text{s}$ ), which means that in TEM on the area occupied by one atom drops  $\sim 10^2 - 10^4$  electrons per second.

The formation of structural defects in materials irradiated by electrons with energies above the threshold energy of radiation-induced defects formation ( $E_T$ ) under irradiation *in situ* in a high-voltage electron microscope ( $E \geq 1 \text{ MeV}$ ) has been well studied for Si, Ge [3,6] and metals [7-9]. The formation of structural defects in ZnS under electron irradiation with above-threshold energies ( $E > E_T$ ) has been insufficiently studied.

The purpose of work was to study the influence of electrons with an energy of 400 keV ( $E > E_T$ ) on the formation of structural defects in ZnS.



## 2. Experimental

Crystals of ZnS with resistivity  $\rho \approx 7 \cdot 10^3 \Omega \cdot \text{cm}$  were prepared using a modified Piper-Polich technique. The crystals were synthesized directly from the vapour phase at a temperature of  $1500^\circ\text{C}$  using polycrystalline starting material, under an argon ambient.

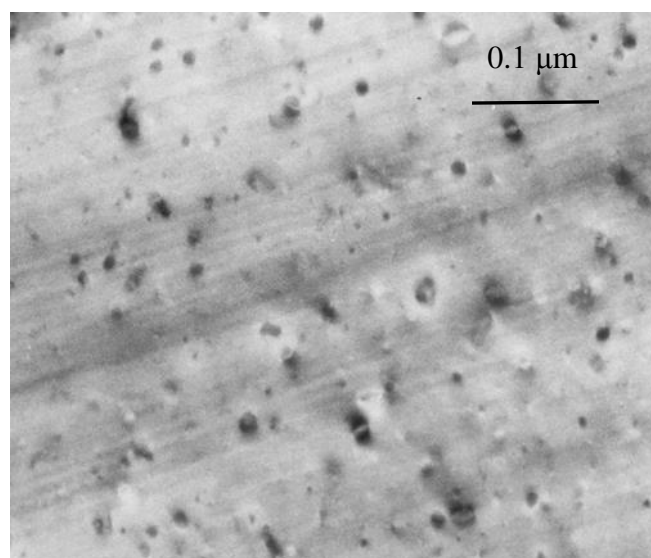
Bulk ZnS crystals were prepared in thin foil form by sequential mechanical polishing and argon ion milling at 5kV, 20 $\mu\text{A}$  and  $15^\circ$  with liquid nitrogen cooling until electron transparent. Improved sample foils were obtained following iodine reactive ion sputtering for 5 to 10 min at 3kV, 10 $\mu\text{A}$  and  $15^\circ$  at room temperature. To completely remove the surface defects formed by ion milling as appropriate thin foil was subjected to chemical polishing for 2-3 seconds in a dilute solution of HPC (a supersaturated solution of  $\text{CrO}_3$  in  $\text{H}_3\text{PO}_4$  heated to  $60^\circ\text{C}$  (1 part), mixed with concentrated  $\text{HCl}$  (2 parts)).

Samples were examined and irradiated in a JEOL 4000EX-II electron microscope operated at 400keV ( $E > E_T$ ) and  $j = 1 - 4 \cdot 10^{19} \text{ e/cm}^2\text{s}$ .

## 3. Results and Discussion

The electron microscopic study of ZnS crystals before irradiation show that they contain of well developed native dislocations and long stacking faults. Also well-developed parallel strips (striations), indicating polytypic modifications of ZnS, are also observed in all cases. This is especially true when the diffraction vector  $\mathbf{g}$  is perpendicular to these strips.

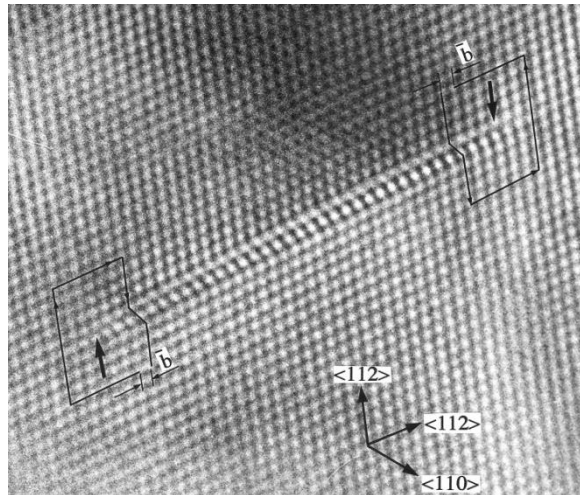
Irradiation of ZnS by electrons with an energy of 400 eV in TEM accompanied by the formation of small dislocation loops. Fig. 1 shows the formation of dislocation loops in ZnS after electron irradiation for 5 minutes. Dislocation loops have a size of 2.5 - 45 nm at a density of  $1.4 \cdot 10^{11} \text{ cm}^{-2}$ . In addition, striations due to the polytype structure of this compound are more readily apparent. The ZnS foil shown in Fig.1 was given a brief chemical polish following  $\text{Ar}^+$  and  $\text{I}^+$  milling to remove the remnant artefact structure.



**Figure1.** TEM image of structural defects in the ZnS irradiated with 400 keV electron beam of intensity  $1 \cdot 10^{19} \text{ e/cm}^2\text{s}$  for 5 minutes.

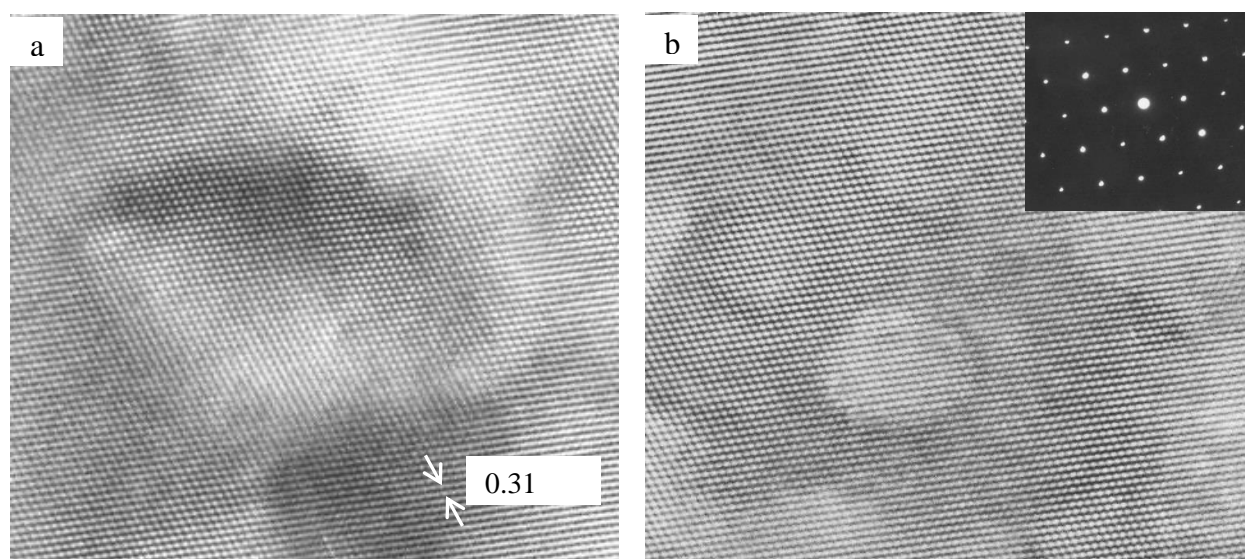
The image with a high resolution (Fig. 2) shows on atomic-scale the formation of dislocation loops in ZnS after electron irradiation. In the image processing has been applied at

least 20 diffracted beams. Extra-planes of dislocations are marked by arrows in Fig. 2. Burgers contours are also drawn. From Fig. 2 follow that the plane of dislocation loop location is the plane  $\{111\}$ , and the Burgers vector of the boundary dislocations is  $\mathbf{b} = a/6\langle 112 \rangle$ .



**Figure 2.** HREM image of 400 keV electron beam irradiated ZnS with intensity  $4 \cdot 10^{19} \text{ e/cm}^2\text{s}$  for 5 minutes

Subsequent electron beam irradiation of ZnS caused growth, transformation, shrinkage and movement of dislocation loops, the formation of new loops, and then the formation of voids. Fig. 3a shows a high resolution plan-view image of dislocation loop formed in ZnS after irradiation for 5 min. In Figure 3b shows the same place after irradiation for 15 minutes. It is seen the formation of voids, which are formed by the accumulation of vacancies, indicating that further decomposition of the material under electron irradiation. At the same time, the crystal structure of the material is preserved, as indicated by electron diffraction pattern obtained from the same place of sample and shown in the upper right corner of Fig. 3b.



**Figure 3.**  $\langle 110 \rangle$  HREM image of 400 keV electron beam irradiated ZnS (the same place of thin foil) with intensity  $4 \cdot 10^{19}$  e/cm<sup>2</sup>s for 5 minutes (a) and 15 minutes (b)

Formations of fine particles size  $\leq 10$  nm with specific moiré fringe contrast were also observed. Creation of modern semiconductor devices of ultra-sizes requires control not only the presence and density of defects such as dislocations, dislocation loops, stacking faults, and microtwins, but also control defects of size of  $\leq 10$  nm. As shown earlier, the formation of new phases in such sizes in materials  $A_2B_6$  possibly under the influence of electrons and ions [10, 11].

Typically, microanalysis of the particles of this size is difficult to technically implement. However, the use of technique moiré contrast, formed from the particles in the high-resolution images, allowing, in certain cases, to determine the chemical composition of these particles. In this case, the period of the moiré contrast  $D$ , occurring when rotating the lattices with the parameters  $d_1$  and  $d_2$  are at an angle  $\alpha$ , can be determined according to [12].

As a result of analysis of fine particles formed in ZnS crystals, irradiated by electrons with energy of 400 keV, was found that the small particles with a moiré fringe contrast can be identified as the phase of  $ZnO_2$ , which is consistent with previous results [1, 10]. So, the decomposition products produced by 400keV electron beam irradiated ZnS is a  $ZnO_2$ . The tendency for the initial formation of oxides of Zn indicates the preferential removal of the anion leading to accelerated oxidation [13].

#### 4. Summary

It was found that the irradiation of ZnS crystals by electrons with energy of 400 keV is accompanied by the formation of dislocation loops, and further shrinkage and movement of loops, the formation of voids and fine particles of the new phase, which can be identified from an analysis of a moiré fringe contrast as  $ZnO_2$ . Regularities of structural defects formation in ZnS can be used to solve problems of management type, density and spatial distribution of defects in the crystal structure, which is important for the implementation of the limiting parameters of microelectronic devices.

### References.

- [1] Loginov Y, Brown P, Durose K *The Regularities of Structural Defect Formation in Semiconductors II–VI* (Logos, Moscow, 2003)
- [2] Kozlovskii V, Lebedev A, Bogdanova E, Seredova N 2015 *Phys. Techn. Semicond.*, **49** 1198
- [3] Aseev A, Fedina L, Hoehl D, Bartsch H *Clusters of interstitial atoms in silicon and germanium* (Akad. Verlag, Berlin, 1994)
- [4] Grushka O, Maslyuk V, Chupyra S, Mysliuk O 2012 *Phys. Techn. Semicond.*, **46** 327
- [5] Lavagne S, Levade C, Vanderschaeve G 2006 *Mater. Science and Engineering: B*, **128** 1
- [6] Hirata M and Kiritani M 1983 *Phys.B.*, **116** 616
- [7] Nakai K, Kinoshita C, Muroo Y, Katajima S 1983 *Phil. Mag. A.*, **48** 215
- [8] Urban K 1979 *Phys. Stat. Sol.(a)*, **56** 157
- [9] Lazarenko V, Platov Y, Pletnev M 1980 *Phys. Metals and Metallography*, **50** 164
- [10] Loginov Y, Brown P, Humphreys C 1995 *Microsc. Semicond. Mater.- Bristol, London: Inst. Phys. Conf.*, **146** 431
- [11] Loginov Yu and Brown P 1992 *Phys. Stat. Sol. (a)*, **132** 323
- [12] Hirsch P, Howie A, Nicholson R, Pashley D and Whelan M *Electron microscopy of thin crystals* (Mir, Moscow, 1967)
- [13] Thangaraj N and Wessels B 1990 *J. Appl. Phys.*, **67** 1535