

## Formation of dislocation loops and voids in electron irradiated zinc selenide single crystals

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**Abstract.** The formation of 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 in size  $\leq 10 \text{ nm}$  in ZnS crystals were found by the transmission electron microscopy method (TEM). Samples were examined and irradiated *in situ* in a JEOL 4000EX-II electron microscope operated at energy of 400 keV and intensity of  $(1 - 4) \cdot 10^{19} \text{ e/cm}^2 \cdot \text{s}$ . Fine particles of a new phase in size  $\leq 10 \text{ nm}$  are formed also. These features can be identified from an analysis of moiré fringe contrast as phase of  $\text{ZnO}_2$ . Similar defects in single crystals of ZnS formed *in situ* after irradiation in a transmission electron microscope JEM-100CX operated at energy of 100 keV and intensity of  $3.5 \cdot 10^{17} \text{ e/cm}^2 \cdot \text{s}$ . It was found that the formation of structural defects in ZnS under electron irradiation with above-threshold energy of defect formation (400 keV) is similar to the formation of structural defects in these crystals under electron irradiation with sub-threshold defect formation energy (100 keV).

### 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 [1-4]. 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, 5] and



metals [6, 7]. The formation of structural defects in ZnS under electron irradiation with above-threshold energies ( $E > E_T$ ) has been insufficiently studied.

Influence of electrons with sub-threshold energies ( $E < E_T$ ) on the processes of structural transformations in semiconductors has been studied in [8-11] where it was reported about possibility of formation of point defects (vacancies and interstitials) in these materials under such irradiation. The formation of structural defects under irradiation of ZnS crystals by electrons with energy  $E < E_T$  in TEM previously discussed in [12]. In the interpretation of the results was used idea about the displacement of the crystal lattice ions under the influence of electrons with sub-threshold energy as a result of the ionization mechanisms of point defects formation based on the known mechanism of Varley [8].

The purpose of this work was to study the influence of electrons with an energy of 400 keV ( $E > E_T$ ) and 100 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 °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 $\mu$ A and 15° 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 $\mu$ A and 15° 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 CrO<sub>3</sub> in H<sub>3</sub>PO<sub>4</sub> heated to 60 °C (1 part), mixed with concentrated HCl (2 parts)). Samples were examined and irradiated in a JEOL 4000EX-II electron microscope operated at 400keV ( $E > E_T$ ) and  $j = (1 - 4) \cdot 10^{19} \text{ e/cm}^2\text{s}$  and JEM-100CX electron microscope operated at 100keV ( $E < E_T$ ).

## 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.

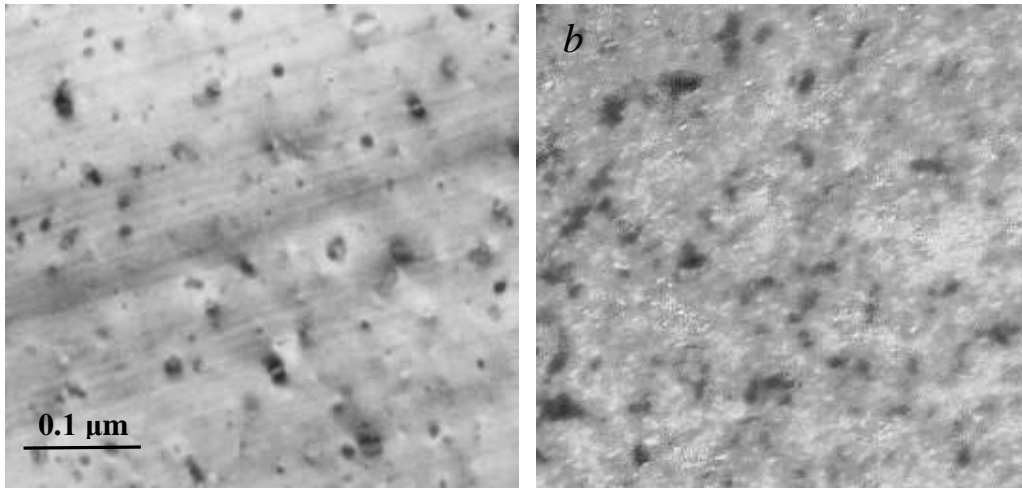
Irradiation of ZnS by electrons with an energy of 400 eV in TEM accompanied by the formation of small dislocation loops. Figure 1,a shows the formation of dislocation loops in ZnS after electron irradiation for 5 minutes. Dislocation loops have a size of 2.5 - 45 nm at a density of  $1.4 \cdot 10^{11} \text{ cm}^{-2}$ . 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 Ar<sup>+</sup> and I<sup>+</sup> milling to remove the remnant artefact structure.

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. Figure 1b shows the bright-field image of ZnS after 15 minutes of irradiation electrons. It is seen the formation of fine voids in the form of bright points of 3-8 nm in size.

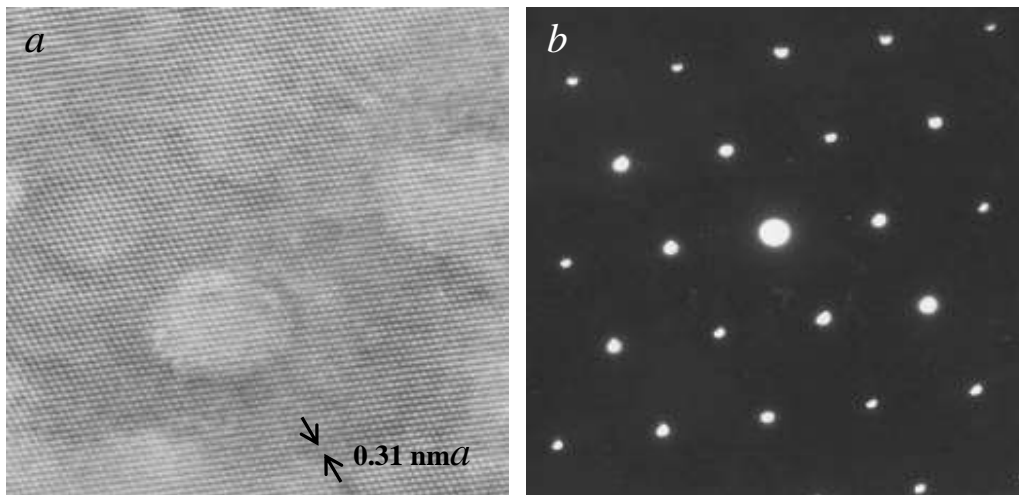
Figure 2,a shows a high resolution image of voids formed in ZnS after irradiation for 15 min. It is seen the formation of voids, which are formed by the accumulation of vacancies, indicating that further decomposition of the material under electron irradiation. At the same time, the crystal structure of the material is preserved, as indicated by electron diffraction pattern obtained from the same place (Fig. 2b).

Formations of fine particles size  $\leq 10 \text{ nm}$  with specific moiré fringe contrast were also observed. Creation of modern semiconductor devices of ultra-sizes requires control not only

the presence 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 [12, 13].



**Figure 1.** TEM image of structural defects in the ZnS irradiated with 400 keV electron beam of intensity  $1 \cdot 10^{19}$  e/cm<sup>2</sup>s for 5 minutes (a) and 15 minutes (b)



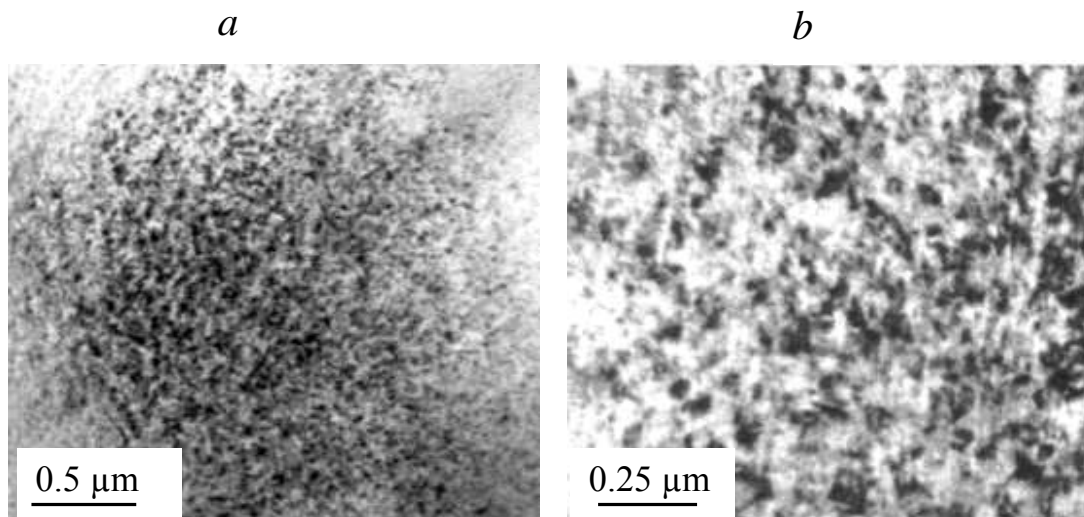
**Figure 2.**  $\langle 110 \rangle$  HREM image of 400 keV electron beam irradiated ZnS with intensity  $4 \cdot 10^{19}$  e/cm<sup>2</sup>s for 15 minutes (a). Diffraction pattern from the same place of thin foil (b)

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 [14]. 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  $\text{ZnO}_2$ , which is consistent with previous results [1]. So, the decomposition products produced by 400keV electron beam irradiated ZnS is a  $\text{ZnO}_2$ . The tendency for the initial formation of oxides of Zn indicates the preferential removal of the anion leading to accelerated oxidation [15].

Similarly to ZnS irradiated by electrons with energy  $E > E_T$ , the irradiation of these crystals by electrons with energies  $E < E_T$  is also accompanied by the formation of dislocation loops and voids.

In Fig.3 shows the formation of structural defects in ZnS irradiated by electron beam with energy of 100 keV for 10 minutes. Defects in the form of small clusters with dark contrast and the dislocation loops are generated first in the center of the irradiated area, and then spread to the periphery. The density of defects increases with the increase of the exposure time. Along with these defects are formed voids with sizes from 3 to 8 nm in diameter, which is clearly seen in Fig.3 b at higher magnification.



**Figure 3.** The formation of structural defects in ZnS irradiated with electrons with energy of 100 keV and the intensity of  $3 \cdot 10^{17} \text{ e/cm}^2\text{s}$  for 10 min.

The final form, concentration and distribution of defects depend on the dose of electron irradiation, the sample temperature and the elastic stress fields. The rate of defect formation is directly proportional to the electron beam intensity, while the final form and density of the secondary defect does not depend on the intensity of exposure. The same patterns are observed in ZnS irradiated by electrons with energies above the threshold energy of radiation-induced defects formation (400 keV).

The experimental data are well explained in the framework of sub-threshold ionization mechanism of defect generation and the subsequent interaction of point defects. Multiple anion ionization causes the formation of Frenkel pairs: interstitial atoms and vacancies. Moderate heating of the sample by the electron beam and the effect of elastic stress fields determine the rate and distribution of secondary structural defects in the irradiated material. Different mobility of interstitial atoms and vacancies creates the possibility of their spatial separation and the formation of vacancy and interstitial clusters. Formation of clusters of point defects in crystals under electron irradiation, in particular, dislocation loops, due to



separation of the components of Frenkel pairs due to different mobilities of vacancies and interstitials.

Voids formation in chalcogenides reflects the fundamental processes of decomposition occurring in the material that is apparently originally associated with atoms of VI group (S) in the formation of interstitial-type clusters with subsequent preferential removal chalcogens from these clusters, as they may exist in the gaseous state and the heat of evaporation is less than the heat of vaporization of Zn atoms. As a result, their place will remain the voids, which will further decorated with a metal phase in the process of migration of Zn atoms on these sinks (or, if the Zn atoms were part of this cluster, they will be concentrated within the void).

#### 4. Conclusion

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<sub>2</sub>.

The phenomenon of the dislocation loops and voids formation in the ZnS crystals under sub-threshold electron irradiation is observed also. The beginning of the formation discernible in the TEM structural defects, the types and concentrations are a function of dose and temperature of electron irradiation and depend on the fields of elastic stresses in the crystal. The experimental data are well explained in the framework of sub-threshold ionization mechanism of defect generation and the subsequent interaction of point defects. A pattern of defects similar patterns of defect formation in these crystals irradiated with electrons with sub-threshold energies. It was found that in the defect formation in the crystals of ZnS irradiated by electrons with energies above threshold along with elastic collisions is significant contributions and inelastic collisions.

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.

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