

DAMAGE TO ZnS FILMS DUE TO NITROGEN ION BOMBARDMENT

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The effect of nitrogen ion bombardment on vacuum deposited ZnS films was investigated by structural and optical techniques. Films, deposited on freshly cleaved mica, have the wurtzite type hexagonal lattice. The film thickness decreases due to the sputtering of the surface layers by the bombarding ions. Decomposition of ZnS to its elemental components is enhanced by the formation of Frenkel pairs as the initially ion bombardment induced defects. Under severe ion bombardment, thermal spikes lead to possible melting and recrystallization.

1. Introduction

When ion beam technology is used, problems arise due to the formation of radiation defects and their effect on the defect sensitive properties of the bombarded substance. Thus, a knowledge of the mechanisms of defect formation and accumulation in ZnS films under ion bombardment is necessary in order to forecast the properties of ion implanted layers and to develop means of controlling these properties.

According to some data the structure of ZnS films is determined by the structure of the original substance^{1,2}), while other data indicate that films condensed on glass are amorphous³) or crystalline of a sphalerite structure⁴) depending on the con-

densation parameters. Recrystallization of ZnS films proceeds differently with annealing^{5,6}). On the other hand, ion bombardment of the films is accompanied by thermal effects; therefore, the question of the structural changes occurring in ZnS films due to the effects of ion bombardment assume considerable importance.

2. Experimental techniques

Pellets of ZnS (99.999% pure) were evaporated from a molybdenum boat by conventional thermal evaporation technique. Pressures during evaporation ranged from 1 to 5×10^{-3} Pa. A deposition rate of about 6 nm/s was used. Film thicknesses were measured interferometrically. The films were deposited on carefully cleaned optically flat glass slides and freshly cleaved mica surfaces kept at room temperature during deposition.

The films were subjected to nitrogen ion beam of current density $800 \mu\text{A} \cdot \text{cm}^{-2}$ extracted from a barrel-shaped orbitron ion source^{7,8}). Structural investigations were carried out by means of X-ray diffraction, electron diffraction and scanning electron microscopy (SEM) techniques. The spectral behaviour of the films was studied in the visible region using a double beam spectrophotometer (Beckmann 5260) and in the infrared region using the double beam spectrophotometer (Beckmann 4220). An interference microscope (POLADUN IV) was used to study the effect of ion bombardment on the interference fringes.

3. Results and discussion

X-ray diffraction study showed that the bulk ZnS used to prepare the films can have both a cubic (sphalerite) as well as a hexagonal type 4H lattice (Wurtzite). Its condensation onto freshly cleaved surface of mica leads to the formation of very fine grain films (grain size of 0.01—0.03 μm). According to the electron diffraction data (Fig. 1 and Table 1) and X-ray diffraction patterns of ZnS films (Fig. 2a), deposited on mica cleavage plane, are polycrystalline corresponding to the wurtzite hexagonal structure with a preferred orientation such that the (100) plane is parallel to the substrate surface. The weaker reflecting line is due to the substrate (008) plate.

The spectral behaviour of as-deposited ZnS films in the visible region indicates that the absorption edge shifts towards higher photon energies as the film thickness increases. Below the absorption edge, interference maxima and minima appear in the case of thick films, in the visible and infrared regions, indicating plane parallel surfaces and homogeneity of the films.

Fig 2b shows X-ray diffraction pattern for ZnS films (200 nm thick, as-deposited) bombarded for 20 minutes. The analysis of this pattern showed the predominance of the (100) plane of the wurtzite structure of ZnS and the (002) plane of metallic zinc. Some reflecting planes corresponding to the mica substrate are also observable. It was observed that the intensity of the (002) plane of metallic zinc and those of the substrate increases on increasing the time of ion bombardment.

This may be taken to indicate two effects of the nitrogen ion bombardment; firstly the decomposition of ZnS monolayers to its elemental components Zn and S, and secondly the reduction of the ZnS film thickness such that the X-rays could pene-

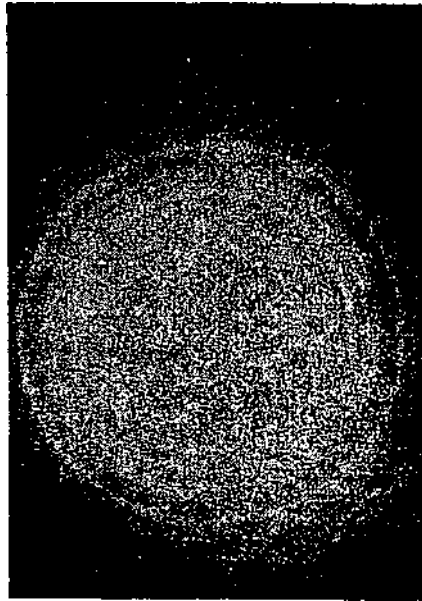


Fig. 1. Electron diffraction pattern of ZnS film, deposited on mica cleavage plane (30 nm thick film).

TABLE 1.

$d_{(obs.)}$ (nm)	ASTM data		Phase
	d (nm)	hkl	
0.2758	0.276	105	Wurtzite
0.2491	0.249	107	Wurtzite
0.1674	0.167	10.16	Wurtzite
0.1464	0.1462	202	Wurtzite
0.1073	0.1072	212	Wurtzite
0.0968	0.0976	214	Wurtzite
0.0912	0.0913	531	Wurtzite
0.0817	0.0824	533	Wurtzite

Transmission electron diffraction data of as-deposited ZnS film on freshly cleaved mica.

trate it and diffracted by the mica substrate. The behaviour of the transmittance of ZnS films after ion bombardment confirms the latter effect, where the transmittance deteriorates and the absorption characteristics of the mica substrate predominates (Fig. 3).

Fig. 4 shows the variation in the spectral behaviour of the optical density of ZnS film (300 nm thick, as-deposited) after ion bombarded for 20 minutes, compared to that before bombardment. The shift of the absorption edge towards long wavelength side and the reduction of the intensity of the interference maxima and minima and their broadness below the absorption edge after bombardment may be taken as criterions for the reduction in thickness. The interested observation is the hump at 765 nm (1.62 eV) which may be due to defective state formed by ion bombardment.

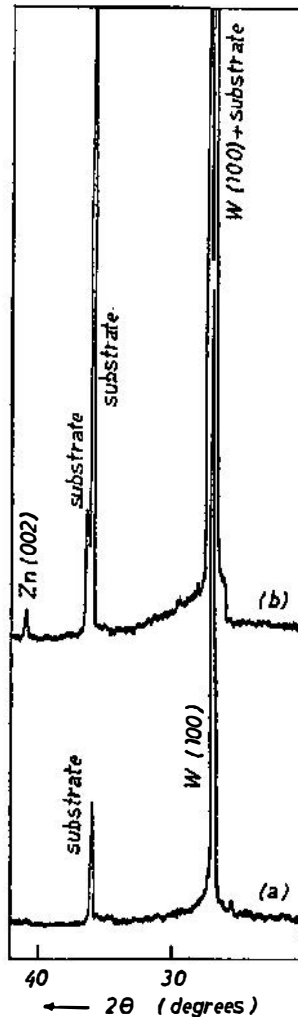


Fig.2. X-ray diffraction pattern of as-deposited ZnS film (200 nm thick) (a) and after being bombarded by nitrogen ions for 20 minutes (b).

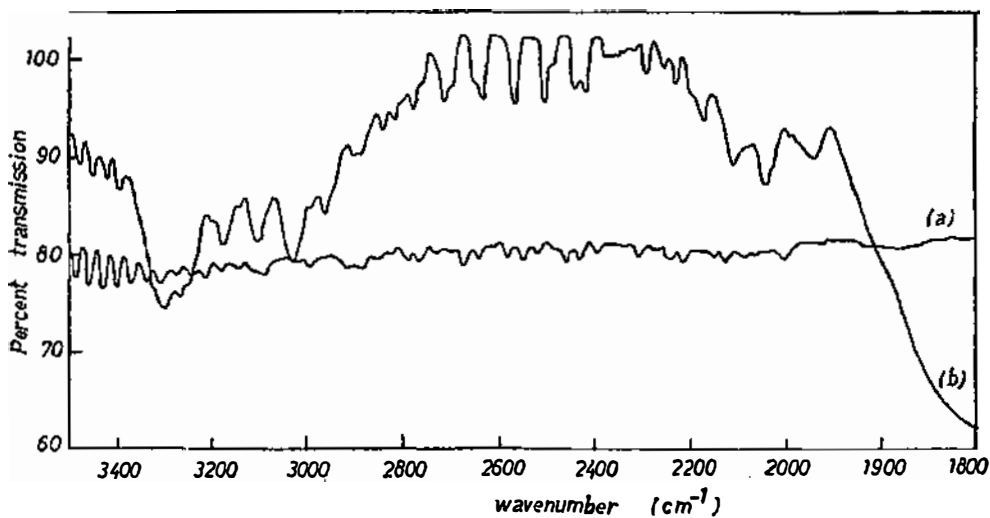


Fig. 3. Spectral variation of percent transmission of a ZnS film in the infrared region before (a) and after ion bombarded (b).

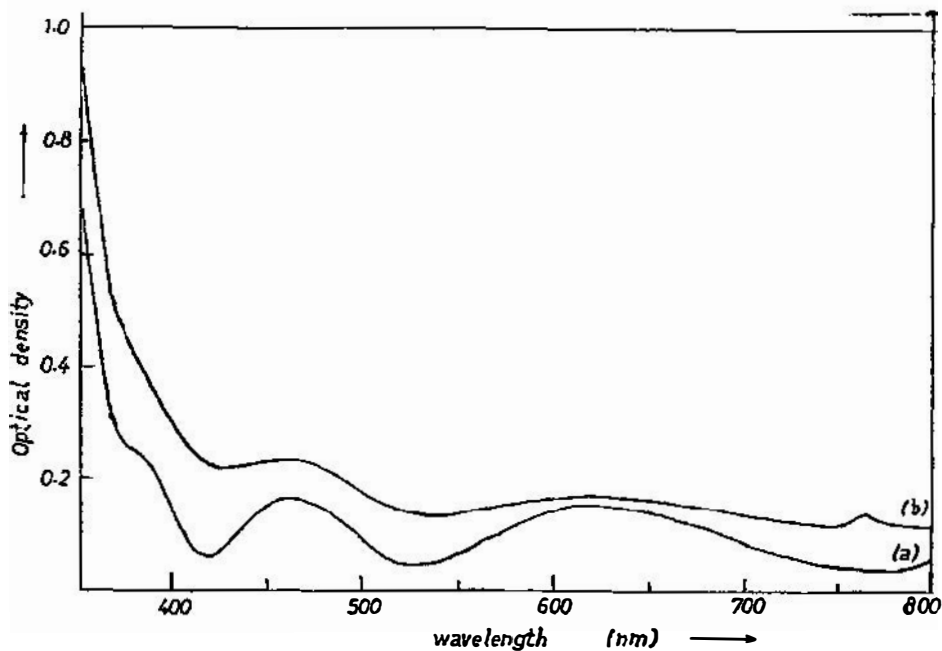


Fig. 4. Spectral behaviour of the optical density (a. u.) of ZnS film (300 nm thick) in the visible region after ion bombardment (a) compared to that before bombardment

Concomitant to the above discussion is the interferograms (Fig. 5) taken for ZnS film deposited on optically flat glass slides at a wedge with a reference reflecting slide coated with silver before and after ion bombardment. The bands are straight and equidistant for as-deposited films indicating that the surface is flat. After ion bombardment, irregular bands, distortions and artifacts of the surface are observable, indicating appreciable deviation of the surface from flatness. In case of multiple

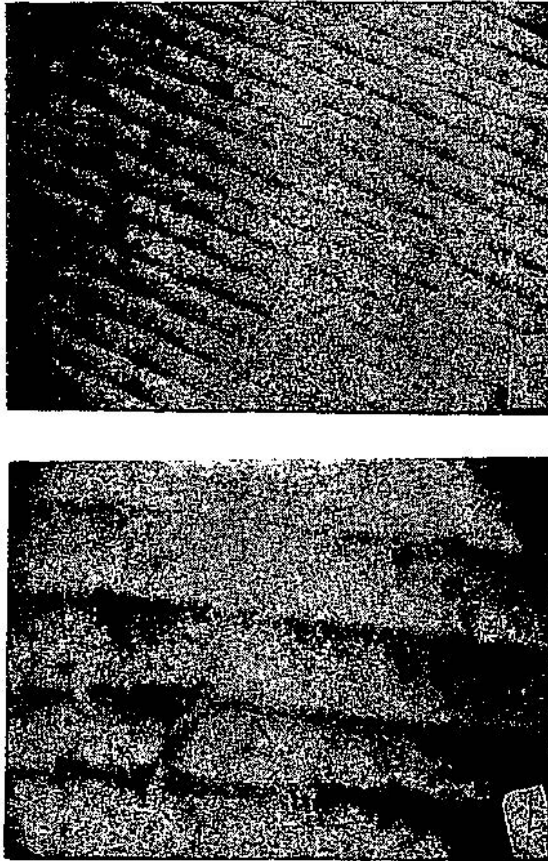


Fig. 5. Interferograms for ZnS film deposited on optically flat glass slide before (a) and after ion bombardment (b).

reflections in plane parallel film⁹⁾, a band for a given $2t \cos\varphi = m$; where t is the film thickness, φ is the angle of light refraction in the film and $m = 0, 1, 2, 3, \dots$ will always be at a place where this condition holds. If t is reduced while φ keeping constant, the band accordingly moves over to the place where the film was thicker. At the initial stages of nitrogen ion bombardment SEM micrographs showed the formation of small spots (dark and bright) (Fig. 6a). The number of such spots, per unit area of the film, decreases with distance from the centre of the bombarded region. The structure of the film around the spots undergoes no changes as the re-

sult of the action of bombardment. The dark spots (microholes) are thought to be caused by localized structural defects which serve as centres at which melting and evaporation of microareas of the film begin. Localized evaporation and the appearance of microholes are also characteristic of ZnS films bombarded by laser beam⁴⁾

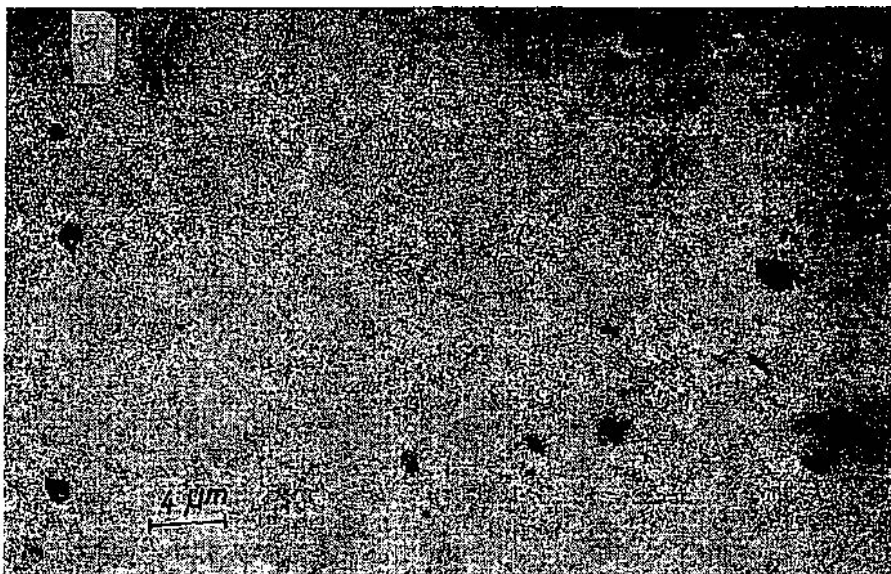


Fig. 6a. SEM micrograph of ZnS film at the initial stage of ion bombardment.



Fig. 6b. SEM micrograph of ZnS film after severe ion bombardment.

and of selenium films bombarded by an electron beam¹⁰⁾. The ion bombardment can lead to the formation of Frenkel pairs (Zn atom interstitial + Zn⁺² ion vacancy). The mobility of Zn interstitial, under bombardment, is more probable and may give to the formation of metallic zinc aggregates which appear as bright areas in SEM micrographs. According to a model proposed earlier^{11,12)} interstitial atoms are more mobile than vacancies. These atoms can recombine with host atoms or with neighbouring vacancies or they may be captured by traps. This is justified in the case of small implantation doses where intrinsic traps are more effective than those associated with radiation induced effects.

Severe ion bombardment has led to local melting and recrystallization of the bombarded area resulting in the formation of different contrasty regions in SEM micrographs (Fig. 6b). The dissipation of excess kinetic energy within the damaged regions results in localised hot spots (thermal spikes). Experiments¹⁴⁾ suggest that the temperature of thermal spikes resulting from ion bombardment is usually within the range 500 to 1000 C and that these last for a maximum duration of about 10^{-11} s, cooling occurring as a result of lattice conduction.

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OŠTEĆENJE ZnS FILMOVA BOMBARDIRANJEM IONIMA DUŠIKA

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U radu se opisuju strukturna i optička istraživanja vakuumski naparenih ZnS filmova izloženih bombardiranju dušikovim atomima. Filmovi su neparivani na kalanu površinu tinjca i imali su heksagonsku, vurcitu rešetku. Za vrijeme bombardiranja, debljina filmova se smanjivala zbog raspršivanja površinskih slojeva i zbog dekompozicije ZnS. Dekompozicija ubrzava formiranje Frenkelovih parova koji nastaju pri početnom bombardiranju. Pod vrlo intenzivnim bombardiranjem javlja se i lokalno zagrijavanje koje vjerojatno uzrokuje taljenje i rekristalizaciju u uzorcima.