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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 a wurtzite-type hexagonal lattice. The film thickness is reduced by the sputtering of the surface layers by the bombarding ions. Under severe ion bombardment, thermal spikes may possibly lead to 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 authors [1, 2], the structure of ZnS films is determined by the structure of the original substance, while other authors indicate that films condensed on glass are amorphous [3] or of a crystalline sphalerite structure [4] depending on the condensation 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 assumes considerable importance.

2. Experimental techniques
Pellets of ZnS (99.999% pure) were evaporated from a molybdenum boat by a conventional thermal evaporation technique. The pressure during evaporation ranged from 1 to 5×10^{-3} Pa. A deposition rate of about 6 nm sec^{-1} was used and 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 a nitrogen ion beam of current density 800 $\mu A\,cm^{-2}$ 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 Beckmann 5260 double-beam spectrophotometer and in the infrared region using a Beckmann 4220 double-beam spectrophotometer. An interference microscope (Poladun IV) was used to study the effect of ion bombardment on the interference fringes.

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

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

3. Results and discussion
X-ray diffraction study showed that the bulk ZnS used to prepare the films can have both a cubic (sphalerite) and a hexagonal-type 4H lattice (wurtzite). Its condensation on to a freshly cleaved surface of mica leads to the formation of very fine-grained films (grain size 0.01 to 0.03 μm). According to the electron diffraction data (Fig. 1 and Table I) and X-ray diffraction patterns

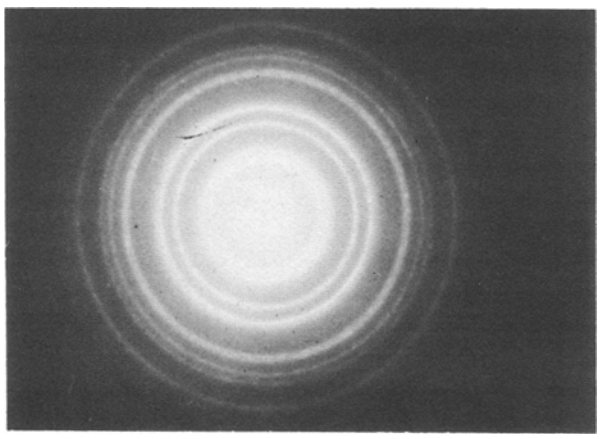

Figure 1 Electron diffraction pattern of ZnS film, deposited on mica cleavage plane (30 nm thick film).

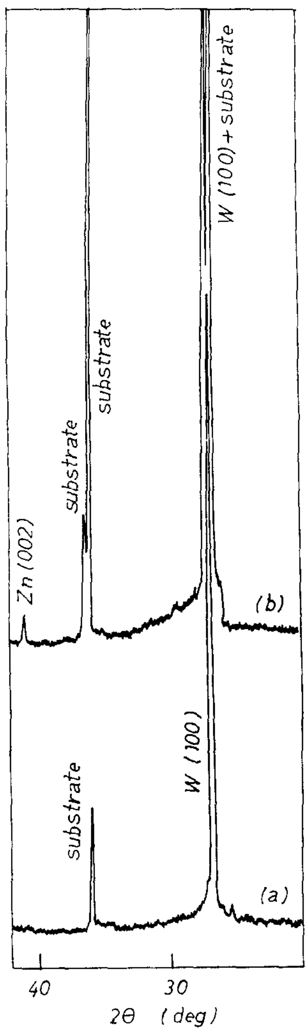

Figure 2 X-ray diffraction pattern of (a) as-deposited ZnS film (200 nm thick) and (b) after being bombarded by nitrogen ions for 20 min.

of ZnS films (Fig. 2a), deposited on a mica cleavage plane, the films are polycrystalline corresponding to the wurtzite hexagonal structure with a preferred orientation such that the (1 0 0) plane is parallel to the substrate surface. The weaker reflecting line is due to the substrate (0 0 8) plane.

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 the X-ray diffraction pattern for ZnS films (200 nm thick, as-deposited) bombarded for 20 min. Analysis of this pattern showed the predominance of the (1 0 0) plane of the wurtzite structure of ZnS and the (0 0 2) plane of metallic zinc. Some reflecting planes corresponding to the mica substrate are also observable. It was observed that the intensity of the (0 0 2) plane of metallic zinc and those of the substrate increases with increasing 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 zinc and sulphur, and secondly the reduction of the ZnS film thickness such that the X-rays could penetrate it and are 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 bombardment for 20 min, compared to that before bombardment. The shift of the absorption edge towards the 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 criteria for the reduction in thickness. An interesting observation is the hump at 765 nm (1.62 eV) which may be due to a defective state formed by ion bombardment.

Concomittant to the above discussion are 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

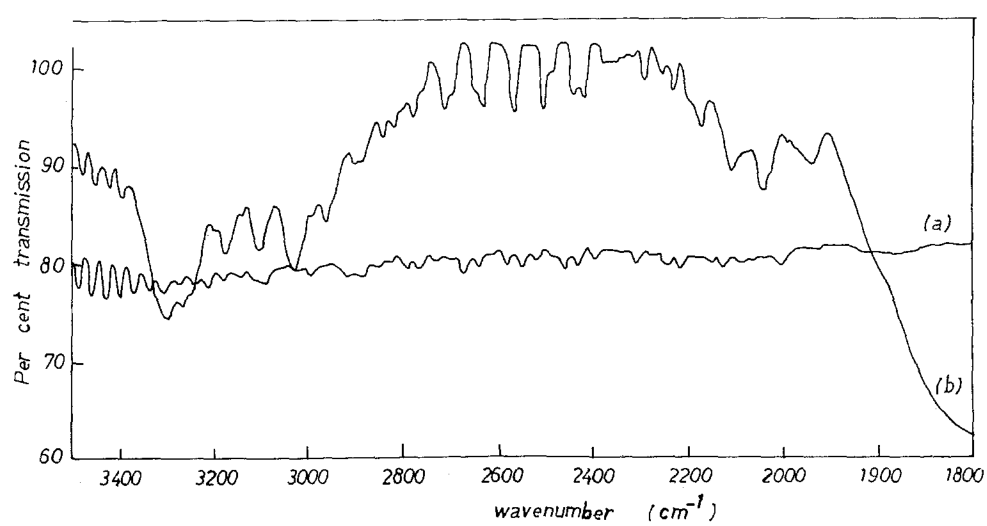

Figure 3 Spectral variation of per cent transmission of a ZnS film in the infrared region (a) before and (b) after ion bombardment.

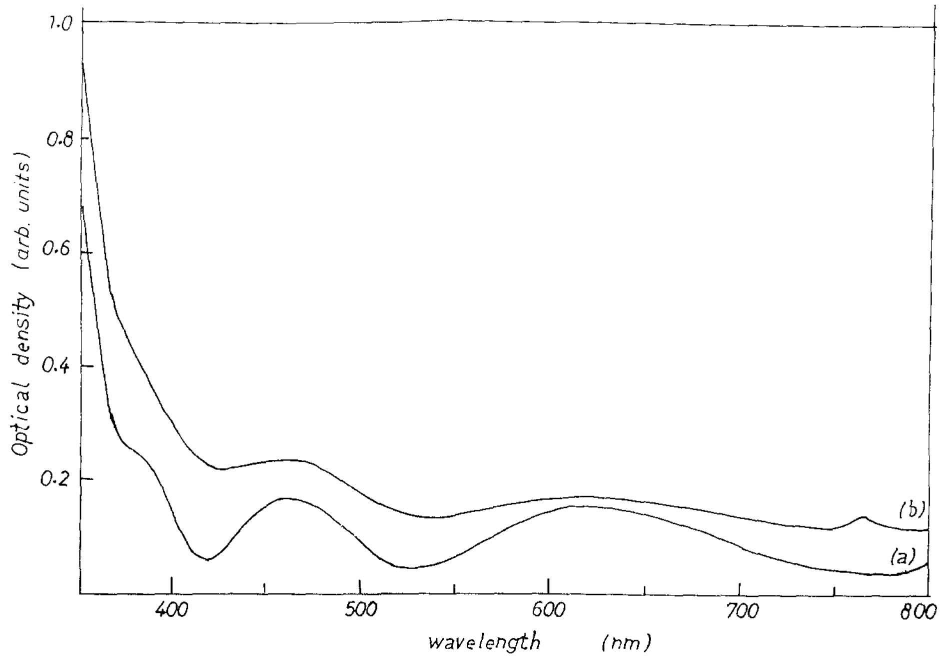

Figure 4 Spectral behaviour of the optical density of ZnS film (300 nm thick) in the visible region (a) after ion bombardment compared to (b) that before bombardment.

for as-deposited films indicating that the surface is flat. After ion bombardment, irregular bands, distortions and artefects of the surface are observable, indicating appreciable deviation of the surface from flatness. In the case of multiple reflections in a plane parallel film [9], a band for a given $2t \cos \theta = m$, where t is the film thickness, θ is the angle of light refraction in the film and $m = 0, 1, 2, 3, \ldots$ will always be at a place where this condition holds. If t is reduced while keeping θ constant, the band accordingly moves over to the place where the film was thicker.

In the initial stages of nitrogen ion bombardment, scanning electron micrographs showed the formation of small spots (dark and bright) (Fig. 6a). The number

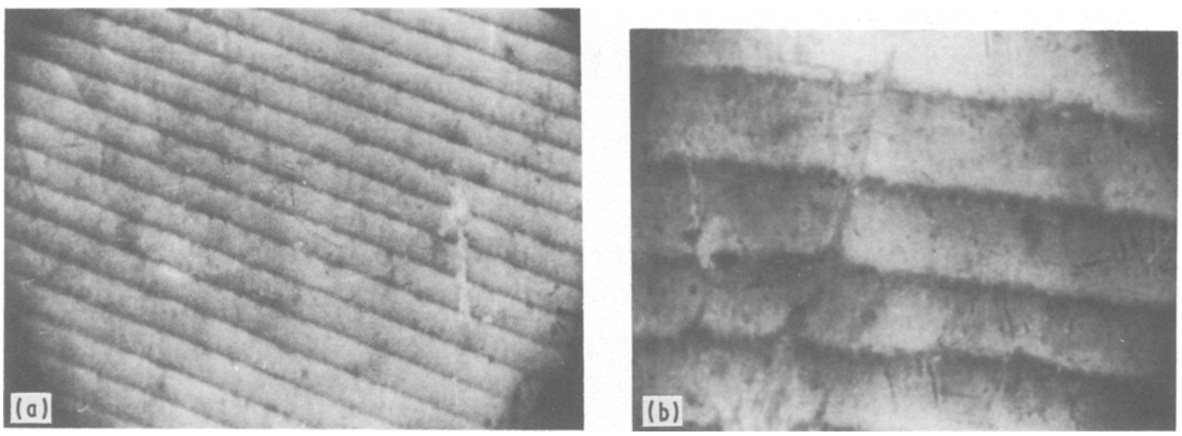

Figure 5 Interferograms for ZnS film deposited on an optically flat glass slide (a) before and (b) after ion bombardment.

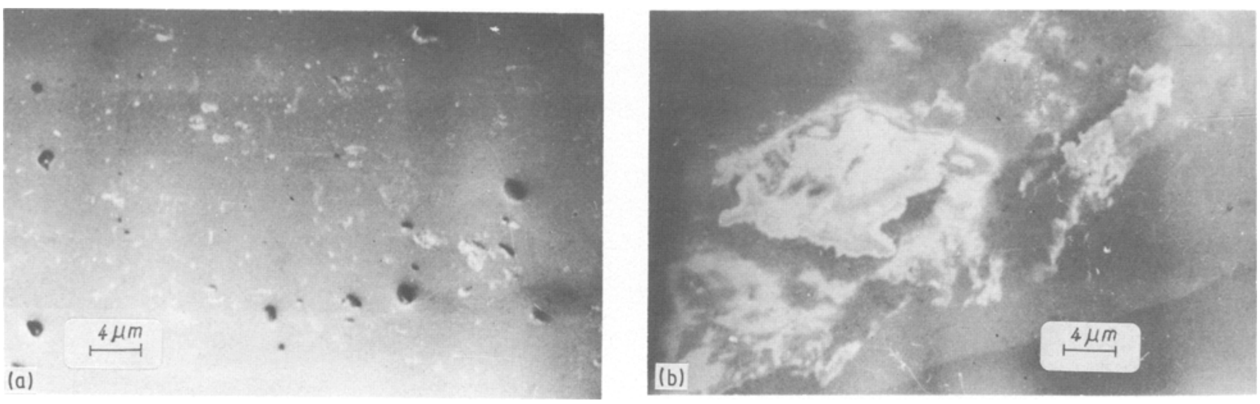

Figure 6 Scanning electron micrographs of ZnS film at (a) the initial stage of ion bombardment, and (b) after severe ion bombardment.

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 change as a result of the bombardment. The dark spots (microholes) are thought to be caused by localized structural defects which serve as centres at which melting and evaporation of micro-areas of the film begin. Localized evaporation and the appearance of microholes are also characteristic of ZnS films bombarded by a laser beam [4] and of selenium films bombarded by an electron beam [10]. The bright spots and their aggregates are thought to be due to metallic zinc.

Severe ion bombardment has led to local melting and recrystallization of the bombarded area resulting in the formation of regions of differing contrast in the scanning electron micrographs (Fig. 6b). The dissipation of excess kinetic energy within the damaged regions results in localized hot spots (thermal spikes). Experiments [11] suggest that the temperature of the 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} sec, cooling occurring as a result of lattice conduction.

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