

Laser damage studies on hot-wall-deposited cadmium selenide films

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II–IV compound semiconductors play a prominent role in modern semiconductor technology. Semiconductor compounds, namely zinc sulphide and zinc selenide in different combinations with other compounds such as magnesium fluoride, thorium fluoride and cryolite are extensively used in producing high-reflecting mirrors and antireflection coatings for lasers, interferometers, cine projector systems [1, 2], etc. The potential of laser irradiation effects in semiconductor materials is already well established [3, 4]. Craighead and Howard [5] and Craighead *et al.* [6] constructed optical information storage cells using thin films of amorphous silicon and amorphous germanium. Kameswara Rao *et al.* [7] have demonstrated novel high-contrast laser imaging based on chemical modification of the surfaces in textured amorphous films of germanium.

Damage can be defined as a permanently induced change in coated optical surfaces. Surface irregularities, pores and cracks cannot be completely avoided even in highly polished surfaces [8]. For laser applications the selection of the material is dependent on properties such as low absorption, high thermal conductivity, minimum change in index with reference to temperature, sufficient hardness, strength, minimum strain and low index. These factors greatly influence the surface damage. The presence of the atmospheric impurities also reduces the surface threshold compared with that of the bulk materials [9]. A clean and polished surface of a transparent medium is not generally more easily damaged than the bulk [10]. The deposition techniques have a high influence on the quality and mechanical resistance of thin films [11]. Since an ideal material does not exist, the selection of a material for laser optics depends on the application and the desired trade-offs.

Laser damage studies on thin films of tantalum oxide [12], cadmium telluride [13], yttrium fluoride [14], cadmium oxide [15], tin oxide and indium tin oxide [16], polymers and Teflon [17, 18], perylene [19], etc., are available in the literature. This letter, for the first time, gives details of the laser damage studies on cadmium selenide thin films obtained by hot-wall deposition (HWD).

Thin films of cadmium selenide (purity, 99.999%; Aldrich Chemical Co., USA) were prepared by the

HWD method. The HWD apparatus was similar to that used by Ramachandran and Vaya [20]. The films were deposited onto well-cleaned glass slides under a vacuum of 6.63 mPa with a vacuum coating unit (Hind Hivac (Bangalore) 12A4). The thicknesses of the films were determined by the gravimetric method using a Metler microbalance. The thicknesses of some hot-wall-deposited samples were verified from the calculations of optical transmittance interference pattern taken using an ultraviolet–visible–near-infrared spectrophotometer (Hitachi U-3400) in the 300–2500 nm wavelength region, which was also used to record absorbance spectra. An X-ray diffractogram with a X-ray generator (PW 1010), a diffractometer (Philips PW 1051) operated at 40 kV and 30 mA with Ni-filtered Cu K α radiation ($\lambda = 0.15418$ nm), a proportional counter and a single-channel pulse height analyser were used for structural analysis of the films.

A schematic diagram of the laser damage experimental set-up is given in Fig. 1. 1.06 μm laser radiation (pulse width, 3 ns; single shot) from a Q-switched Nd-doped yttrium aluminium garnet laser (Quanta Ray DCR-11) was focused to a diameter of about 1 mm using a convex lens (focal length, 19 cm) onto the surface of the sample kept away from the focal point of the lens. The laser energy

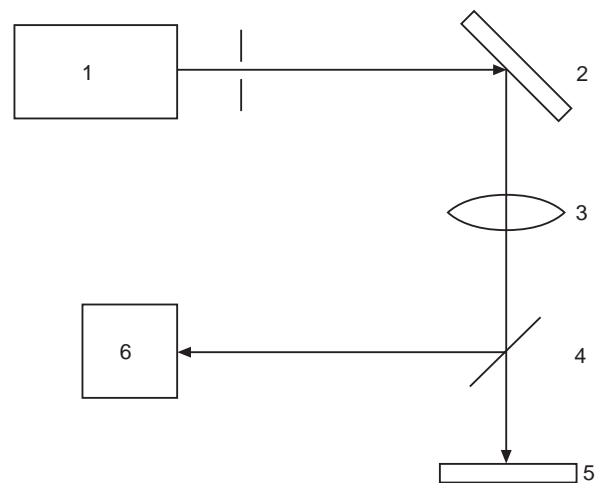


Figure 1 Schematic diagram of laser-induced damage threshold measurements. 1, Nd-doped yttrium aluminium garnet laser; 2, mirror; 3, lens; 4, beam splitter; 5, sample; 6, energy meter.

was measured for each laser pulse using an on-line pulsed-laser energy meter (Delta Developments), triggered in synchronization with the laser pulse. The distance of the sample from the lens was kept constant throughout the study and the laser output energy was varied. Each data point was taken with the laser pulse falling on a fresh surface of the sample by moving the sample horizontally. To begin with, the first shot with energy above 40 mJ impinging on the film damaged it; it was visualized from the appearance of a bright white spark which melted a small volume of the material and hence incurred total damage. Since a well-defined threshold damage was needed [21] the energy was slowly reduced for the subsequent shots. Once the damage threshold was attained, there was no further damage to the film with further reduction in the impinging laser energy. The damage sites were examined with an optical microscope and the threshold damage location was identified. From the measured energy and the area of damage, the threshold energy density was calculated.

The films deposited by the HWD technique were found to have a wurtzite polycrystalline structure with highly preferred orientation along the (002) direction (Fig. 2). Table I shows the variation in the threshold energy density with thickness and the structural and optical parameters of hot-wall coated films. It has been observed that the threshold energy density increases with decrease in film thickness.

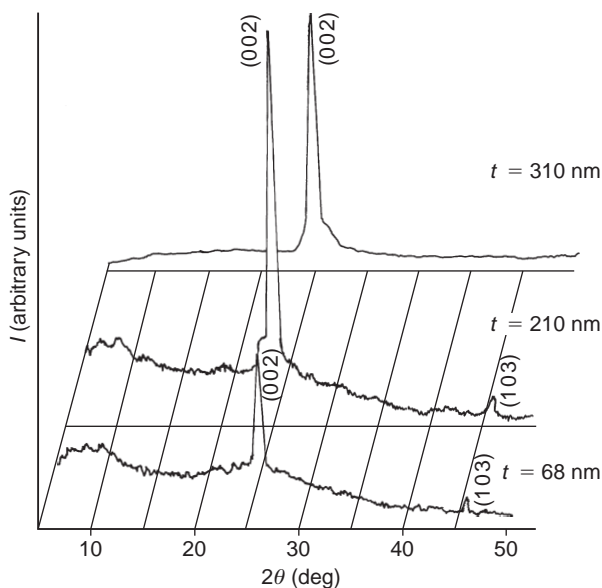


Figure 2 X-ray diffraction pattern of hot-wall-deposited cadmium selenide thin films of 68 nm, 210 nm and 310 nm thicknesses.

This can be explained by using the impurity-dominated model proposed for dielectric films. In this model a small spherical particle on the surface of the film absorbs energy from the incident radiation. This absorption produces an increase in the temperature of the particles at that particular point, leading to melting, vaporization or stress fracture of the material around the impurity. Similar trends were reported for yttrium fluoride [14], perylene [11] and germanium [22] films.

Since the laser damage studies were carried out in normal atmospheric air, the presence of atmospheric impurities markedly influences the damage threshold values, favouring surface absorption. At low energies, the damage induced by the laser is only on the surface layers, causing cracks and slight damage as depicted in Fig. 3. However, at higher energies the damage has the aspect of real “craters”, like the sputtering of material itself (Fig. 4).

From the X-ray diffractogram, the crystalline size, D (obtained using Scherrer's formula [24]), the dislocation density, δ , and strain, ϵ (evaluated from the formula given by Williamson and Smallman [24]), were evaluated (Table I). The absorption coefficient was calculated from the relation [25]

$$\alpha = \frac{\log A}{t}$$

where A is the absorbance obtained from the absorption spectrum and t is the thickness of the film.

From Table I the thickness dependence of the threshold density is seen explicitly. It was observed that, as the thickness increases, the grain size increases and the strain and dislocation density

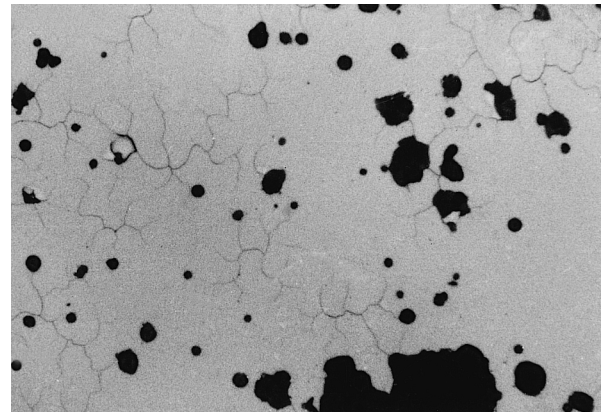


Figure 3 Threshold damage site of a hot-wall-deposited cadmium selenide thin film. (Magnification, 60 \times .)

TABLE I Dependence of the damage threshold energy density on the thickness, crystallite size, D , dislocation density δ , strain, ϵ , and absorption coefficient, α , of hot-wall-deposited CdSe thin films

Thickness (nm)	Threshold energy density (J m^{-2})	D (nm)	δ ($10^{14} \text{ lin m}^{-2}$)	ϵ ($10^{-4} \text{ lin}^{-2} \text{ m}^{-4}$)	α (10^5 m^{-1})
68	0.95	18.5	29.2	19.4	0.92
210	0.87	26.3	14.45	11.8	4.45
310	0.83	28	12.7	10.5	8.57

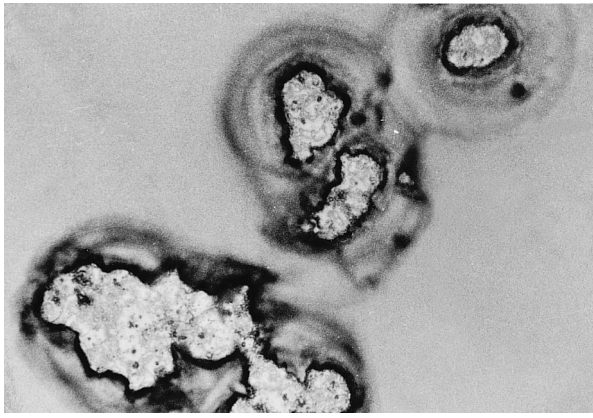


Figure 4 Full damage site of a hot-wall-deposited cadmium selenide thin film showing sputtering of the material. (Magnification, 90 \times .)

decrease. The decrease in the damage threshold energy density can be explained on the basis of the increase in the absorption coefficient, α , with increase in the film thickness. The increase in the thickness increases the grain size and hence the absorption. The higher the absorption, the lower is the threshold damage density, as observed by earlier workers for indium tin oxide [16] and germanium films [22].

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