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Photon, electron and ion beam induced physical and optical densification in chalcogenide films

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Abstract. Irradiation of 80° deposited Se-Ge films with band gap photons, 8 keV electrons and 50 keV He^+ ions produces, primarily irreversible red shift of the absorption edge and major changes in doping and electrochemical adsorption processes. These changes have been attributed predominantly to the radiation-induced thickness and hence volume contraction resulting due to the physical collapse of the low density columnar microstructure of the obliquely deposited films. The far IR and Urbach tail studies reveal an enhanced strength of electron-phonon coupling, in obliquely deposited films having a very porous columnar microstructure, compared to normally deposited films. It has been shown that this enhanced electron phonon coupling is conducive to large thickness contraction and associated changes. These changes have been used in reprographic and lithographic applications. A correlation has been established between the thickness contraction and lithographic parameters. The possibility of generating both positive and negative relief patterns on the same film by controlling the etching time has been demonstrated.

Keywords. Chalcogenide films; optical densification.

1. Introduction

Thin films of amorphous Se-Ge have been shown to behave as inorganic resists for visible, UV and deep UV light as well as electron beam and ion beam exposures and possess many advantages over the conventional organic resists currently in use (Yoshikawa *et al* 1976, 1977, 1980; Tai *et al* 1979; Balasubramanyam *et al* 1981; Venkatesan 1981). Using the light, electron beam or ion beam induced doping, or the darkening effects, both negative and positive type resists can be realized. Extensive studies carried out in our laboratory have shown that very large thickness and hence volume contraction (physical densification) takes place in $Se_{75}Ge_{25}$ films deposited at 80° incidence and exposed to photons, electrons or ions (Singh *et al* 1979, 1980a; Chopra *et al* 1981, 1982). The thickness contraction results in a much larger darkening in these films, compared to that obtained on exposure of films deposited at normal incidence. Thickness contraction occurs also when $Se_{75}Ge_{25}$ films overcoated with a very thin (100–200 Å) layer of a metal, such as Ag, are irradiated. This affects the doping of Ag into the chalcogenide film. Both the positive and negative resist behaviour of the obliquely deposited films are expected to be different from that of the normal incidence films and to be correlated with the thickness contraction resulting in these films on irradiation. In the present study, we have examined this correlation and utilized it to (a) yield a better lithographic sensitivity and contrast, both for the negative and positive resist behaviour, and (b) obtain both positive and negative resist characteristics in the same film.

2. Experimental

The experimental details for vacuum deposition of amorphous Se-Ge films are the same as reported earlier (Singh *et al* 1979; Rajagopalan *et al* 1979). The films were masked with a sharp edge and exposed to photons and ions. A 250 W mercury vapour lamp with an intensity of 30 mW/cm^2 was used for band gap photon illumination. Ion (He^+) irradiation was carried out with a 50 keV ion beam, using an ion accelerator (Sames J-15) in a vacuum of 10^{-7} torr, at room temperature. No ion sputtering or deformation of the film occurred during irradiation. The films were irradiated with an 8 keV, 0·2 μm diameter electron beam (PHI 590-A Super SAM instrument) for electron beam exposures. The thickness contraction was determined by measuring the thickness difference between the exposed/irradiated and the unexposed/unirradiated regions with the help of Talystep and then normalized against the original starting thickness of the as-deposited film.

For studying the negative resist behaviour, thin layers of Ag and Cu, (about 200 Å thick), were deposited on the as-prepared Se-Ge films by electrochemical adsorption (dipping in 0·025 M $AgNO_3$ 1 M $CuSO_4$ respectively) as well as by thermal evaporation. The resulting metal-Se-Ge films were then irradiated with photons, electrons and ions in the same way as described above and the thickness contraction was determined. The chemical dissolution rates of the films, with and without the metal overlayer, were determined by developing the films in 0·25 M NH_4OH solution.

3. Results and discussion

A comparison of the thickness contraction brought about by the irradiation of the 80°-deposited $Se_{75}Ge_{25}$ films by photons, electrons and ions is shown in figure 1. A

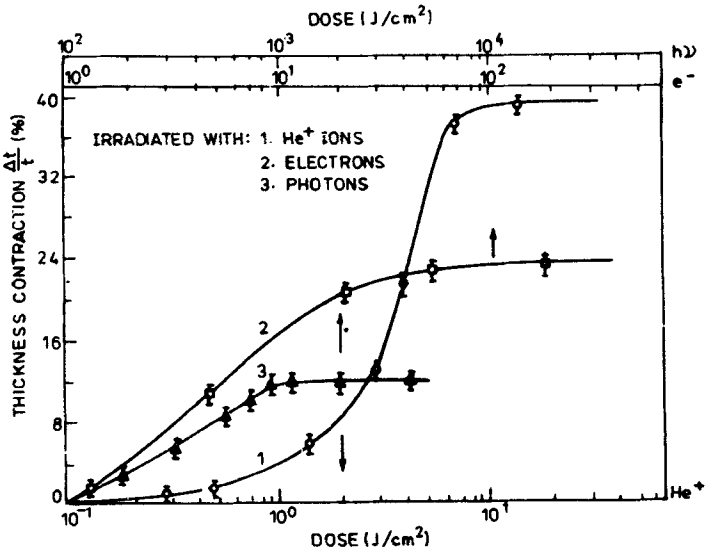

Figure 1. Thickness contraction as a function of incident flux for photon, electron and ion beam-irradiated 80°-$Se_{75}Ge_{25}$ films.

comparison of the incident energy reveals that ions are more effective in bringing about contraction followed by electrons and then photons. It may be pointed out that calculations of projected range and range straggling for He^+ ions in $Se_{75}Ge_{25}$ film show that there is no ion implantation in the film since the film thickness is smaller than the projected range.

The as-deposited Se-Ge films dissolve readily in an alkaline solution. The solubility is increased on irradiation. For $Se_{75}Ge_{25}$ films deposited at normal incidence, the increase in the solubility is rather small and hence not a very useful effect. The large thickness contraction occurring in 80° films leads to large microstructural changes which in turn increases the solubility difference between the irradiated (contracted) and unirradiated regions (Singh *et al* 1980b). The dissolution rates can be obtained from figure 2 which shows the normalized remaining thickness *vs* normalized etching time (*i.e.* the time taken to remove a certain thickness of an irradiated or a virgin film divided by the total time taken for the complete removal of the irradiated or the virgin film) for an as-deposited and irradiated (with ions, electrons and photons) $Se_{75}Ge_{25}$ film. Two kinds of etching selectivity are obtained as a function of the etching time. In the initial stages of etching, the unexposed regions etch faster than the exposed regions, *i.e.*, a negative resist behaviour is obtained even without the use of an overlayer metal. The etching behaviour changes to a positive resist type (exposed portion dissolving faster than the unexposed portion) after a certain etching time which is higher for photons and comparatively much lower for electrons and ions. If the etching is stopped when the exposed or irradiated portion has been completely etched off, the fractional final thickness remaining in the unirradiated or unexposed portion is about 88% for the ion irradiated, 78% for electron irradiated and 33% for photon irradiated films. A comparison of this data with that reported by earlier workers reveals that a much higher remaining thickness is obtained by us (Yoshikawa *et al* 1976, 1977; Tai *et al* 1979;

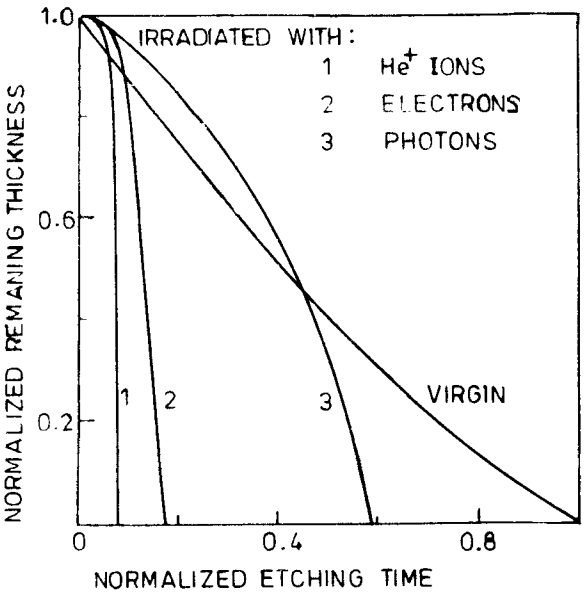

Figure 2. Normalized remaining thickness *vs* normalized etching time for a virgin and irradiated (with ions, electrons and photons) 80°-$Se_{75}Ge_{25}$ films.

Balasubramanyam *et al* 1981; Venkatesan 1981). Thus the value of 33% obtained in photon-irradiated films in the present case is much higher than 13% reported by Yoshikawa *et al* (1976), in normal incidence $Se_{75}Ge_{25}$ films obtained by sputtering. The difference can be attributed to the large thickness contraction obtained in the 80° films and absent in normal incidence films. Similarly, the large value of 88% in the ion-irradiated case obtained in the present study is much higher than 58% reported by Balasubramanyam *et al* (1981), on obliquely deposited films of the same material possibly due to the larger thickness contraction in our films resulting from the use of heavier He^+ ions. Thus, a control of etching time can permit both positive and negative relief patterns to be generated on the same film.

Figure 3 shows the normalized remaining thickness *vs* ion dosage corresponding to an etching time just sufficient for the complete removal of the exposed portion. As mentioned above; a very large selective etching of 88% has been obtained. A contrast (γ) of 4·5 and sensitivity (S) $\sim 10^{-4}$ C/cm^2 have been obtained. Though the sensitivity is lower than the conventional organic resists, the large selective etching and a reasonably good value of contrast make the films suitable for positive resist applications. Typical values of the lithographic parameters for positive resist applications for different radiations are listed in table 1.

Negative resist characteristics are obtained when the films with an overlayer of Ag or Cu are irradiated with ions, electrons or photons. Figure 3 shows our results on the negative resist characteristics for He^+ irradiated Se-Ge films with an overlayer of Ag. A sensitivity $\sim 1{\cdot}4 \times 10^{-5}$ C/cm^2 and a contrast of 8·3 have been obtained. The negative resist characteristics for different radiations obtained by this process are also listed in table 1. The high value of contrast should produce a high intrinsic resolution in these films for ion beam lithographic applications. Submicron lithographic patterns have been generated by us and other workers routinely (Balasubramanyam *et al* 1981; Venkatesan 1981; Chopra *et al* 1982).

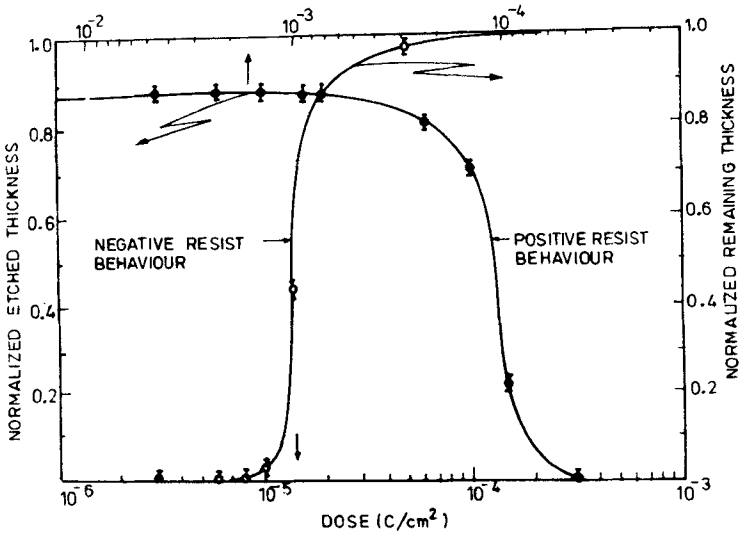

Figure 3. Positive and negative resist characteristics of 80°-$Se_{75}Ge_{25}$ films subjected to He^+ irradiation.

Table 1. Lithographic parameters (sensitivity, S, and contrast, γ) for different radiations for 80°-$Se_{75}Ge_{25}$ films.

Radiation	As-positive resist		As-negative resist	
	S	γ	S	γ
He^+ ions	$\sim 1{\cdot}2 \times 10^{-4}$ C/cm^2	4·5	$\sim 1{\cdot}6 \times 10^{-5}$ C/cm^2	8·3
Electrons	$\sim 8 \times 10^{-4}$ C/cm^2	4	$\sim 1 \times 10^{-4}$ C/cm^2	7·6
Band gap photons	$\sim 10^{20}$ photons/cm^2	1·7	$\sim 10^{19}$ photons/cm^2	3·5

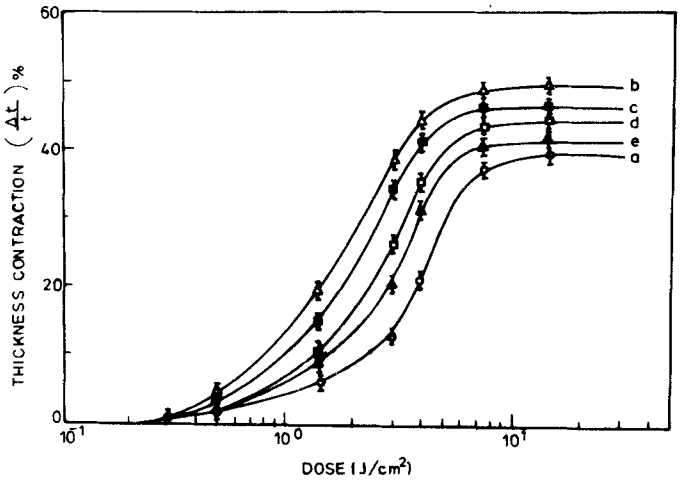

Figure 4. Thickness contraction as a function of ion dosage for: **a.** as-deposited, **b.** as-deposited with an overlayer of electrochemically adsorbed Ag, **c.** as-deposited with an overlayer of evaporated Ag, **d.** as-deposited with an overlayer of electrochemically adsorbed Cu, and **e.** as-deposited with an overlayer of evaporated Cu.

Our studies show that the thickness contraction plays an important role in the negative resist action in the obliquely deposited films. Figure 4 shows the thickness contraction as a function of ion dosage for: (a) as-deposited, (b) as-deposited with an overlayer of electrochemically adsorbed Ag, (c) as-deposited with an overlayer of evaporated Ag, (d) as-deposited with an overlayer of electrochemically adsorbed Cu, and (e) as-deposited with an overlayer of evaporated Cu. It is noteworthy that the thickness contraction is larger in a film having an overlayer of a metal than in one without an overlayer. The improved negative resist characteristics in obliquely deposited films is therefore a direct consequence of enhanced thickness contraction.

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