Novel laser induced image storage by chemical modification of surfaces in *in situ* textured amorphous Ge films[a]

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(Received 6 May 1986; accepted for publication 10 July 1986)

A novel high-contrast laser imaging based on chemical modification of the surfaces has been demonstrated in textured amorphous films of Ge. The process of imaging has been studied by x-ray initiated Auger electron spectroscopy, x-ray photoelectron spectroscopy, transmission electron microscopy, and microdensitometry. Laser irradiation transforms amorphous Ge and amorphous GeO phases to crystalline Ge and GeO phases, the GeO phase growing at the cost of the Ge phase. This leads to imaging, the contrast of which can be enhanced by annealing in air at 525 °C. Photoenhanced chemical modification of the surfaces with concomitant topological rearrangements of the irradiated network has been suggested as the phenomenon responsible for imaging in these films. Such chemical modification of the surfaces has a large potential in high-resolution high-contrast laser imaging.

The potential of laser irradiation effects in semiconductor materials is well established.[1-4] When irradiated with short pulse laser beams, these materials undergo various structural and chemical transformations.[1,2] The present interest in such reactions is stimulated by the recent investigations of Craighead *et al.*[5,6] on optical information storage in thin films of amorphous Si (*a*-Si) and amorphous Ge (*a*-Ge). These workers have demonstrated[5,6] that by irreversibly altering the absorption properties of microscopically textured *a*-Si and *a*-Ge surfaces, a large optical contrast between the irradiated and unirradiated regions can be achieved. Furthermore, the sensitivity of the textured films is found to be higher compared to the nontextured films. However, in all these studies, the textured films were prepared in a separate batch by reactive ion etching of the surface before subjecting them to laser irradiation. A critical control over the process parameters during etching is essential which limits the versatility of the technique.

The surface and volume texture of several semiconducting films can also be tailored by suitably adjusting the deposition parameters during the film growth. Recent studies on obliquely deposited films suggest[7,8] that the angle of deposition is a predominant factor in establishing several of the surface features. Films deposited at an oblique angle of incidence exhibit pronounced columnar microstructure. The properties of these textured films differ in many respects[7] from the nontextured films. To our knowledge, no attempt has so far been made to exploit the image storage potential of such *in situ* textured films. In the present study we have therefore investigated this image storage potential in obliquely deposited *a*-Ge films. Since 80° deposited films show predominant surface texture, the present investigations were carried out on 80° deposited Ge films. This letter reports the results of these investigations.

Thin films of *a*-Ge of thickness ~ 5000 Å were deposited on glass in vacuum $\sim 10^{-6}$ Torr at 80° incidence. A pulsed free-running Nd:YAG laser (1.06 μm) at an intensity of 9 kW/cm^2 and a pulse width of 300 μs was used in the present study. The absorption coefficient (α) of the films is $\sim 10^3$–10^4 cm^{-1} for the wavelength of the laser radiation (1.06 μm) producing the chemical change. The optical penetration depth is therefore $\sim 10^5$–10^4 Å, which is much greater than the film thickness. To enhance the image contrast after irradiation, the films were annealed at a temperature of 525 °C in air for 30 min. Al K_α x-ray photoelectron spectroscopy (XPS) and x-ray initiated Auger electron spectroscopy (XAES) studies were carried out in ESCA-3 Mark II spectrometer of VG Scientific Ltd. The structural and mi-

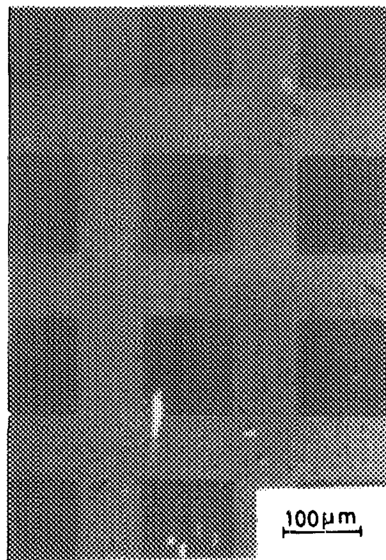

FIG. 1. Optical micrograph of the replicated image of a TEM grid pattern by laser irradiation and annealing.

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crostructural studies were carried out using Phillips EM 301 transmission electron microscope (TEM) with films of thickness < 1000 Å. The optical density of the films was measured using a microdensitometer.

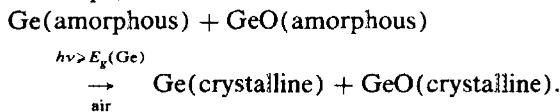
Figure 1 shows the optical micrograph of the image of a 200 mesh TEM grid pattern on an 80° deposited Ge film, replicated by laser irradiation and annealing. The films were annealed only to enhance the already existing optical contrast between the irradiated and unirradiated regions and hence is not mandatory. The information can be read directly after writing since the image contrast before annealing is sufficient to be detected by any commercially available laser diodes. A grey scale has also been achieved due to spatial variations in the incident light intensity.

We propose the following mechanism for imaging in 80° deposited amorphous Ge films.

Step (i) Exposure to atmospheric air

$$\text{Ge(amorphous)} \xrightarrow{\text{air}} \text{Ge(amorphous)} + \text{GeO(amorphous)}.$$

Step (ii) Nd:YAG laser irradiation

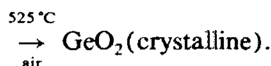


$$\text{Ge(amorphous)} + \text{GeO(amorphous)} \underset{\text{air}}{\xrightarrow{h\nu > E_g(\text{Ge})}} \text{Ge(crystalline)} + \text{GeO(crystalline)}.$$

Step (iii) Annealing at 525 °C

(a) Regions which are laser irradiated undergo no change;

(b) Regions which are unirradiated transform as



$$\text{Ge(amorphous)} + \text{GeO(amorphous)} \underset{\text{air}}{\xrightarrow{525\,^{\circ}\text{C}}} \text{GeO}_2\text{(crystalline)}.$$

Exposure of 80° deposited films to atmospheric air leads to the formation of traces of amorphous GeO phase [step (i)]. The peak at a kinetic energy (KE) of 1146 eV [Fig. 2(a)] corresponds to pure Ge (Ge^0) and the peak at a KE of 1139.5 eV corresponds to GeO (Ge^{2+}) phase.[9] The XPS spectrum [Fig. 3(a)] indicates two binding energy (BE) peaks for Ge ($2P_{3/2}$) level. The BE peak at 1216.5 eV corresponds to pure Ge (Ge^0) and the peak at 1219.5 eV corresponds to GeO (Ge^{2+}).[9] The formation of traces of GeO phase may be due to the predominant columnar microstructure of large apparent density deficit[8] and hence the tendency for passivation of the dangling bonds by atmospheric oxygen as is evident from the XAES and XPS data.

Irradiation of the films containing amorphous phases of Ge and GeO, with photons of energy greater than the band gap of Ge, facilitates the breaking of the Ge–Ge bonds, creating unsaturated bonds at the Ge sites. Photo-oxidation of these sites leads to the growth of GeO phase at the expense of Ge phase. This is shown both in the Ge (L_3VV) XAES [Fig. 2(b)] and Ge ($2P_{3/2}$) XPS spectra [Fig. 3(b)]. The phases Ge and GeO are both crystalline [step (ii)].

On annealing, regions that have been laser irradiated, containing crystalline phases of Ge and GeO, do not undergo any change [step (iii)(a)]. However, regions that have not been irradiated, containing amorphous phases of Ge and GeO, transform to GeO_2 which is crystalline [step (iii)(b)]. In Fig. 2(c), the KE peak in the Ge (L_3VV) region shifts from 1146 eV (Ge^0) to 1137.2 eV. This 8.8 eV shift in the Ge (L_3VV) region is a "fingerprint" of the formation of the GeO_2 phase (Ge^{2+}).[10] Similarly, the BE peak of Ge ($2P_{3/2}$) level in Fig. 3(c) shifts from 1219 eV (corresponding to GeO) to 1220 eV again indicating the formation of GeO_2.[10]

The XAES and XPS results are supported by our transmission electron microscope investigations. Figure 4 shows the electron micrograph of the as-deposited film. The corresponding diffraction pattern characterized by the structureless haloes indicating the amorphous nature of the film is shown in the inset. Figure 5 shows the electron micrograph and the corresponding diffraction pattern after the film is subjected to laser irradiation. Every ring in the diffraction pattern can be associated either with cubic Ge or with hexag-

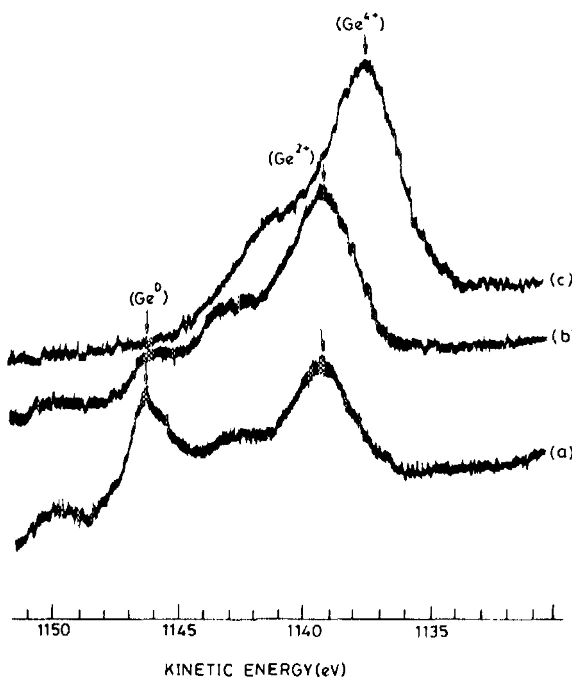


FIG. 2. Ge (L_3VV) XAES spectra of the films (a) before and (b) after laser irradiation, and (c) after annealing.

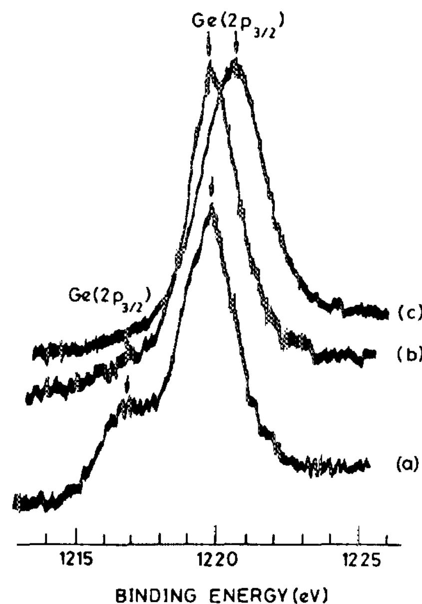


FIG. 3. Ge ($2P_{3/2}$) XPS spectra of the films (a) before and (b) after laser irradiation, and (c) after annealing.

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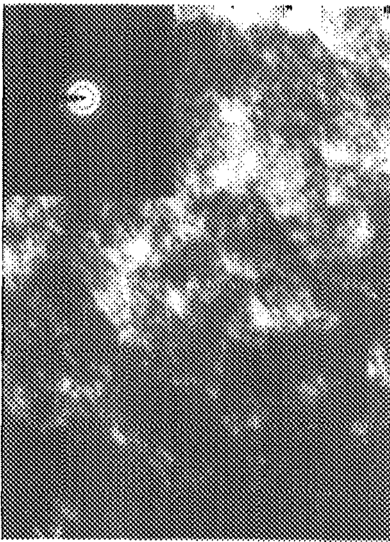

FIG. 4. TEM micrograph with the corresponding diffraction pattern of the films before laser irradiation.

onal or tetragonal GeO_2, except those with the "d spacings," 3.800, 2.925, and 2.730 Å. However, XAES and XPS data clearly indicate that on irradiation the GeO_2 phase is completely absent and it is the GeO phase which grows at the expense of the Ge phase. All the diffraction rings in the TEM data of Fig. 5 must therefore arise from crystalline phases of Ge and GeO and not GeO_2.

The electron micrograph with the corresponding diffraction pattern of the film which is annealed in air at 525 °C after irradiation is shown in Fig. 6. The "d spacings" calculated from the diffraction pattern indicate the formation of a mixture of hexagonal and tetragonal phases of GeO_2 in conformity with the XAES and XPS results. Also evident is a gross rearrangement of the microstructural features of the films after irradiation (Fig. 5) and annealing (Fig. 6).

The structural, microstructural, and chemical modifications in the films are accompanied by corresponding changes in the optical density measured in the visible region. The optical density in the unirradiated and irradiated regions are 1.07 and 1.72, respectively. These correspond to effective transmittance values of 8.5% and 1.9%, respectively. The optical density values, after annealing at 525 °C, are 0.09 and 1.58 in the unirradiated and irradiated regions, respectively. These correspond to effective transmittance values of 81% and 2.6%, respectively. Thus, the irradiated regions do not undergo any significant changes in transmittance on annealing (1.9–2.6%) whereas the unirradiated films show enormous changes in transmittance (8.5–81%). Since the as-deposited films are amorphous (Fig. 3) in nature, with no grain size limitations, the intrinsic resolution of the material is extremely high ($\lesssim 100$ Å), limited only by the range of photogenerated carriers. Although the 1.06 μm laser (Nd:YAG) used in the present study limits the writing spot size, shorter wavelengths in the ultraviolet and visible regions could also be used for effecting changes leading to imaging. Thus, besides offering a very large potential for high-contrast laser imaging, the obliquely deposited films are textured *in situ*. Furthermore, the process of photo-oxidation demonstrates the possibility of using such textured films for high-resolution microfabrication. It also broadens the possible range of useful optical storage media.

FIG. 5. TEM micrograph with the corresponding diffraction pattern of the films after laser irradiation.

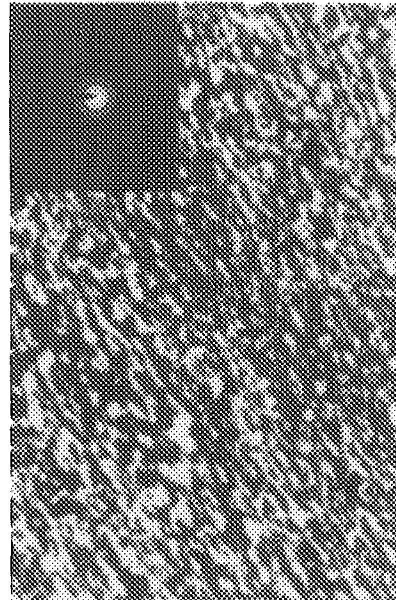

FIG. 6. TEM micrograph with the corresponding diffraction pattern of the films after annealing.

In summary, we have demonstrated a novel high-contrast laser imaging based on chemical modification of the surfaces in textured a-Ge films. Photo-oxidation of Ge, a rearrangement of the textured microstructural features, and the underlying amorphous→crystalline transformation have been suggested as factors responsible for imaging.

The authors would like to thank Professor E. S. Raja Gopal for his encouragement and G. N. Subbanna for help in electron microscopy work.

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