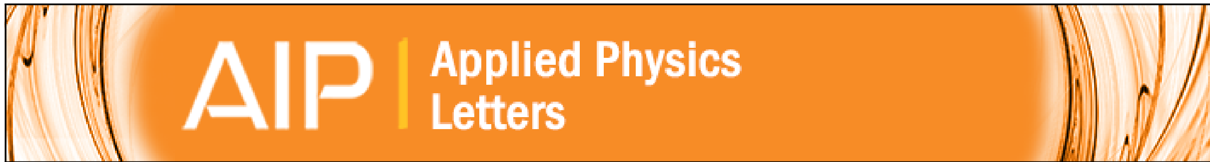

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M. Mulato, A. R. Zanatta, D. Toet, and I. E. Chambouleyron

Citation: Applied Physics Letters **81**, 2731 (2002); doi: 10.1063/1.1512307
View online: http://dx.doi.org/10.1063/1.1512307
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Optical diffraction gratings produced by laser interference structuring of amorphous germanium–nitrogen alloys

M. Mulato[a)]
Departamento de Física e Matemática, Faculdade de Filosofia Ciências e Letras de Ribeirão Preto, Universidade de São Paulo, Av. Bandeirantes 3900, Ribeirão Preto, SP, Brazil

A. R. Zanatta
Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, SP, Brazil

D. Toet
FlexICs Inc., 165 Topaz Street, Milpitas, California 95035

I. E. Chambouleyron
Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas-Unicamp, Campinas, SP, Brazil

(Received 13 June 2002; accepted 13 August 2002)

We use the interference of two pulsed laser beams (wavelength = 355 nm) to produce an optical diffraction grating in amorphous germanium–nitrogen alloy (*a*-GeN). At the constructive maxima of the interference pattern, the absorption of light leads to crystallization. The crystallized region results of pure microcrystalline germanium (μc-Ge). An indication that Ge–N bonds have broken and nitrogen outdiffused of the film is obtained from infrared spectroscopy and confirmed by Raman spectra. A pattern of alternating *a*-GeN and μc-Ge lines with a period of about 4 μm acts as an optical diffraction grating due to the difference in optical properties between the two materials, and the three dimensional surface profile, caused by N_2 effusion, that is formed on the sample. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1512307]

Laser processing is a technology of growing interest in the semiconductor industry.[1–19] Short pulse laser crystallization of amorphous semiconductors, in particular, has attracted a lot of attention since it enables the fabrication of high performance polycrystalline devices on low temperature substrates, for example, for flat panel display applications.[9–11] Experimental and theoretical studies have shown that laser crystallization involves ultrafast melting and solidification processes occurring far from thermal equilibrium.[12–17] Bringing two laser beams to interference on the surface of an amorphous film results in a sinusoidal modulation of the light intensity and leads to a pattern consisting of alternating amorphous and polycrystalline lines (dots are obtained when three beams are used). This technique was first demonstrated on hydrogen-free amorphous silicon (*a*-Si) in 1994,[18] and later on hydrogen free amorphous germanium (*a*-Ge),[12,15] and is very promising for controlled grain growth and reduced lithographic processes in industrial applications, among others.

Amorphous silicon and germanium films typically contain more than 10 at. % hydrogen when grown by plasma enhanced chemical vapor deposition. This is undesirable for laser crystallization, since the rapid heating caused by the absorption of the laser radiation results in explosive effusion of the hydrogen. This leads to disruption of the film surface, causing roughness, and, in the case of *a*-Ge:H, the formation of a free-standing film.[19] A controlled hydrogen effusion by oven or low-fluency laser anneal is necessary to overcome this problem.

In this work, we study the pulsed laser crystallization of hydrogen-free amorphous germanium–nitrogen alloys (*a*-GeN). We discuss the role of nitrogen during phase transitions and the possible application of the resulting structure as an optical diffraction grating, when two laser beams are used for the interference structuring of the sample.

The samples of the present work were produced by the rf sputtering technique, using a germanium target in an Ar $+N_2$ atmosphere.[20] The nitrogen partial pressure during deposition was 7×10^{-3} mbar and the total pressure 15 $\times10^{-3}$ mbar. The dc bias was 640 V. Corning 7059 glass and *c*-Si bar substrates were used, and held at 230 °C during deposition. Typical samples are 0.5 μm thick. The nitrogen concentration in the alloy is about 30%.[20]

In Fig. 1, the spectral transmittance[21] of an *a*-GeN sample (solid line) is compared to that of the glass substrate and that of a typical *a*-Ge:H sample. The higher optical gap of *a*-GeN is apparent from the figure.[20] Other physical properties of *a*-GeN, as well as those of *a*-GeN:H alloys can be found in the literature.[20,22–25]

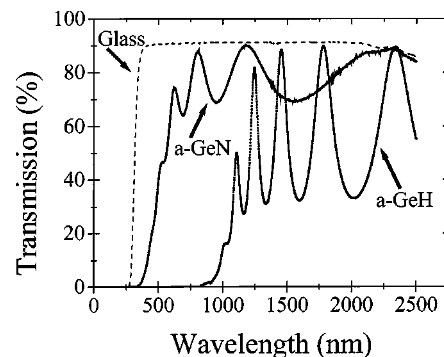

FIG. 1. Optical transmission spectra of glass, *a*-GeN and *a*-Ge:H samples.

[a)]Electronic mail: mmulato@ffclrp.usp.br

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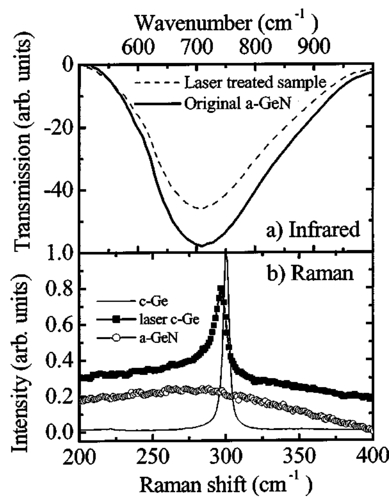

FIG. 2. (a) Infrared Ge–N stretching absorption band of an *a*-GeN film, solid line: as-deposited sample; dashed line laser treated sample. (b) Raman spectra of a reference *c*-Ge (111); as-deposited *a*-GeN; and laser crystallized *a*-GeN samples.

The samples were treated by a single shot of either one or two simultaneous 10 ns laser pulses (150 mJ/cm^2) of the third harmonic (355 nm) of a Nd-YAG laser. For the production of the gratings, the laser output was split into two beams which were then brought to interference at the surface of the sample. Time resolved experiments were not performed for monitoring the laser processes, which were performed at room temperature in air.

Figure 2(a) shows the relative intensity of the absorption band corresponding to the asymmetric Ge–N stretching vibration mode of an as-deposited *a*-GeN sample (solid line). The dashed line in the same figure indicates the strength of the same absorption band after laser irradiation. It is apparent from Fig. 2(a) that, after crystallization, the total number of Ge–N bonds has decreased in the sample. The area ratio indicates a loss of around 23%. This result suggests that nitrogen has either effused from the sample or is trapped inside the germanium matrix as N_2 molecules. As discussed next, nitrogen effusion seems to be the most plausible effect, in a way similar to the explosive effusion of hydrogen in Si:H (Ge:H) alloys upon laser crystallization.

Figure 2(b) shows the results of Raman backscattering experiments performed using the 488 nm wavelength of an argon laser. The figure displays the spectra of a control *c*-Ge (111 oriented) sample, an as-deposited *a*-GeN film, and a laser crystallized *a*-GeN sample, respectively, as solid line, circles, and squares. The difference between the control *c*-Ge and the as-deposited *a*-GeN sample, which does not show any peak, can be clearly seen in Fig. 2(b). The *c*-Ge spectrum shows a peak corresponding to the TO-phonon, at 300 cm^{-1}. A similar peak also appears in the laser crystallized samples. However, the crystallized samples present a broader signal and a Raman shift smaller than *c*-Ge. This indicates that the laser treated sample consist of a distribution of small crystallites rather than a monocrystalline Ge film.

The top part of Fig. 3 shows a two dimensional surface profile, measured by atomic force microscopy (AFM), of an *a*-GeN film exposed to two interfering beams. The top figure corresponds to a surface image of the sample, while the bottom figure corresponds to a horizontal scanning along the surface, thus leading to a vertical profile that helps analyzing the three dimensional nature of the sample. The darker lines in the top picture of Fig. 3 correspond to the laser crystallized part of the sample, resulting in a μc-Ge strip, while the clear (and broader) lines are unaffected by the laser and remain amorphous GeN. The white circular dots appearing in Fig. 3 (top) correspond to defects of the original sample and are not related to the laser treatment.

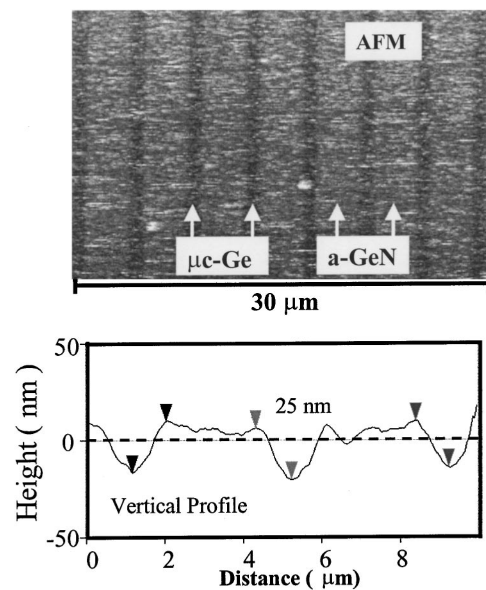

FIG. 3. AFM measurements of the line pattern of an *a*-GeN laser irradiated film using two interfering beams. Top: surface profile; bottom: vertical profile corresponding to a horizontal scanning along the top image. The hills correspond to *a*-GeN and the valleys to μc-Ge. Note the height variation of about 25 nm between the valley and the top of the hills. The line period is about 4 μm.

The profile shown in the bottom part of Fig. 3, which corresponds to a horizontal scan across the lines, indicates that the crystallized portion of the film is lower than the amorphous part by about 25 nm. This can be explained by a partial ablation of the Ge film caused by explosive laser-induced nitrogen effusion, analogous to what occurs in the case of hydrogen in *a*-Si:H. Note that no formation of a free-standing membrane was observed in the present case, contrary to what was found in hydrogenated Ge samples. We believe that the laser irradiated lines are not crystallized through the whole thickness of the sample. Instead, only a thin surface layer of the sample might be converted to μc-Ge, whereas the bottommost part of the same lines still remains *a*-GeN. More investigations are needed to confirm this hypothesis.

The particular structure of the sample, shown in Fig. 3, having a line period of around 4 μm with a line width of about 1 μm, can be used as an optical diffraction grating because it combines two effects: the different surface optical properties of the two materials (μc-Ge and *a*-GeN) and a three dimensional profile of the lines.

In order to check this possibility, we used a He-Ne laser beam (633 nm) with a circular profile, and measured the diffracted pattern at a distance of 20.5 cm from the sample. The resulting diffraction pattern was photographed and is shown in Fig. 4. The distance between the maxima was used to calculate the diffracted angle θ, and used in the equation:

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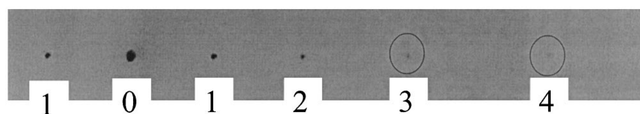

FIG. 4. Digital photograph of the diffraction pattern of a He-Ne laser beam ($\lambda = 633$ nm) with a circular spot. The snapshot of the diffracted beams was taken with the grating shown in Fig. 3 at a distance of 20.5 cm from the sample. The numbers identify the diffraction maxima (m). The distances from $m = 0$ are 3.4, 7.0, 11.3, 17.3, and 27.8 cm for $m = 1$, 2, 3, 4, and 5, respectively. A grating period of 3.92 ± 0.03 μm is thus obtained.

$$d \sin \theta = m\lambda, \tag{1}$$

where d is the grating period, λ is the wavelength of the incident light, and m is the number of the diffraction maximum, to obtain d. From the experiment, the resulting grating period was $d = 3.92 \pm 0.03$ μm, in agreement with the AFM measurements.

In summary, the present letter reports on the consequences of nitrogen effusion in laser processed *a*-GeN alloys, which behaves in a way similar to that of hydrogen in laser irradiated Si and Ge hydrogenated alloys. As a consequence of nitrogen effusion, the crystallized surface of *a*-GeN results in a pure μc-Ge region of a reduced thickness. This thickness difference and the different optical properties of the crystallized and the amorphous regions was found to behave as an efficient optical diffraction grating, with a line period of around 4 μm under the present experimental conditions. Further experiments based on the analysis of the integrated intensity of the interference maxima are needed to distinguish which is the main physical effect.

The authors are indebted to Dr. P. V. Santos (PDI-Berlin) for his participation in the early stages of this work, to their colleagues for fruitful discussions, and to E. de Paula for experimental help. This work has been supported by the Brazilian agencies FAPESP and CNPq.

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