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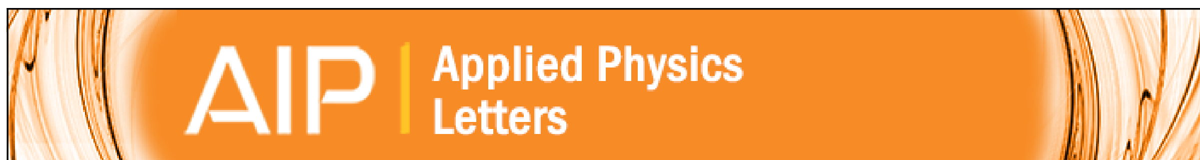

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Laser crystallization and structuring of amorphous germanium

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The short-pulse laser crystallization and interference structuring of amorphous germanium films were investigated by time resolved reflection measurements and Raman spectroscopy. We demonstrate that submicrometer crystalline structures with very sharp lateral interfaces can be produced by laser interference crystallization of nonhydrogenated samples. In hydrogenated films, on the other hand, the film surface disrupts upon laser exposure leading to the formation of a free-standing crystalline membrane. The Raman spectra of laser crystallized germanium display effects of finite crystallite size and stress. © *1997 American Institute of Physics.*
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Laser crystallization (LC) is gaining increasing importance in the fabrication of polycrystalline silicon thin films used for instance in thin film transistors.[1] This is mainly due to the fact that LC enables the production of high quality layers on low-cost substrates such as glass and plastics. In combination with interference techniques, LC can also be used for the creation of microstructures for applications in electronic and photovoltaic devices.[2] This technique, called laser interference crystallization (LIC), has been successfully applied to the production of microcrystalline line and dot gratings on amorphous silicon films (a-Si).[3,4]

In this letter, we report on laser-induced crystallization and structuring of a-Ge and its hydrogenated counterpart (a-Ge:H) using short laser pulses (ns range). LC a-Ge films find potential applications as infrared detectors and tandem solar cells. Most of the published work on LC of a-Ge used cw or long laser pulses (ms range), despite the successful use of short laser pulses for the crystallization of a-Si films for large area electronics.[5,6] Thin films of amorphous semiconductors with electronic quality require the incorporation of hydrogen into the amorphous network; detailed information on the LC kinetics of these films is still missing. In order to gain insight into the role of hydrogen, we also studied a-Si and a-Si:H samples. The crystallization process was investigated by time-resolved reflection measurements (TRR), and the structure of the crystallized materials was studied by Raman spectroscopy.

The 1-μm-thick a-Ge samples were grown by rf sputtering, the hydrogenated ones having 8% bonded hydrogen, as determined from the integrated area of the wagging Ge–H infrared absorption band.[7] The 300-nm-thick silicon samples were grown by low pressure chemical vapor deposition (LPCVD) and by plasma enhanced chemical vapor deposition (PECVD). The PECVD samples contain 15% bonded hydrogen; the LPCVD ones almost none. The samples were crystallized using single pulses (7 ns wide, intensities up to 300 mJ/cm^2) of a frequency doubled Nd:YAG laser ($\lambda = 532$ nm). The crystallization was monitored *in situ* by measuring the change in reflection of a HeNe laser beam ($\lambda = 632.8$ nm) impinging on the sample at an incidence angle of 68°. The laser exposures were performed at room temperature and atmospheric pressure.

TRR profiles obtained during laser crystallization of a-Ge (pulse energy of 48 mJ/cm^2) and a-Si (300 mJ/cm^2) films are shown in Figs. 1(a) (curve LC) and 1(c), respectively. In both cases, the TRR signal initially increases to a value corresponding to the reflection coefficient of the melted phase[8] and falls off as the sample cools down. The maximum reflection is independent of the laser energy for

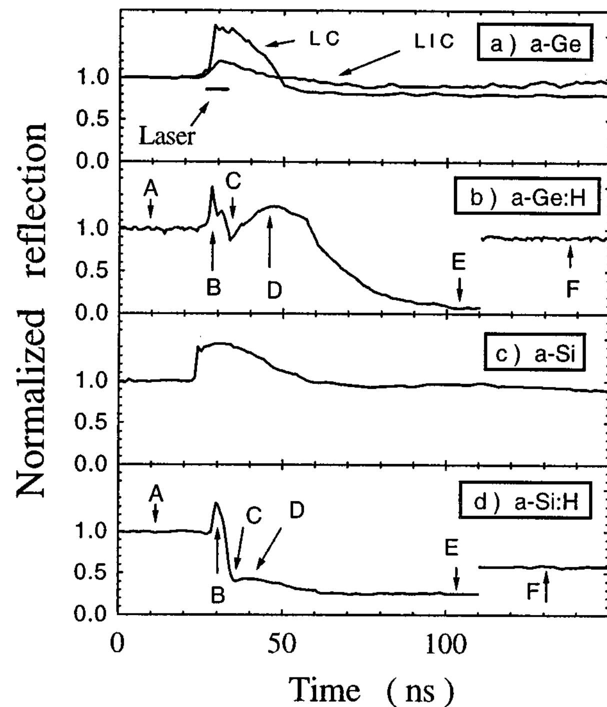

FIG. 1. Time resolved reflectance, during laser crystallization of: (a) a-Ge (pulse energy of 46 mJ/cm^2), (b) a-Ge:H (38 mJ/cm^2), (c) a-Si (300 mJ/cm^2), and (d) a-Si:H (64 mJ/cm^2). The arrows and letters indicate different stages of the crystallization process. The horizontal line in (a) displays the duration of the laser pulse and F indicates the reflection after cleaning the sample with an air flow. The LIC line in Fig. 1(a) was measured during interference crystallization using three laser beams.

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energies above the melting threshold. Amorphous germanium crystallizes at smaller laser pulse energies (crystallization threshold of 36 mJ/cm^2) than a-Si (threshold of 95 mJ/cm^2), as expected from the higher absorption coefficient and the lower melting temperature.

A striking phenomenon observed during the laser crystallization of the hydrogenated Ge samples is the fact that the top part of the film lifts off, forming a thin free-standing membrane (area of $\sim$ 1 mm^2). This is illustrated in Fig. 1(b), which shows the TRR of an a-Ge:H sample crystallized with a pulse of 38 mJ/cm^2. During laser irradiation, the reflection increases to a maximum indicated by point B, attributed to the formation of a melted layer on the sample surface. Between B and C the signal decreases following a complicated pattern. The same behavior is observed for a-Si:H samples [see Fig. 1(d), energy of 64 mJ/cm^2]. The decrease in the signal at point C is attributed to a disruption of the film surface caused by hydrogen effusion. The disrupted surface scatters the HeNe beam out of the TRR detector. In the case of a-Ge:H, however, we observe a recovery of the TRR signal (point D). The recovery is attributed to the formation of a smooth crystallized membrane, loosely attached to the underlying amorphous film. As a consequence, the heat cannot be conducted away from the irradiated layer as rapidly as in nonhydrogenated films [Fig. 1(a)] and thus the TRR signal decreases more slowly. Upon cooling, the membrane lifts off, leading to a reduction of the TRR signal (point E). After removing the membrane from the film surface using compressed air, the TRR signal reaches the value indicated by F.

The thickness of the lifted off c-Ge membrane was inferred by:

(i) the analysis of the optical transmission spectrum[9] before and after the laser treatment;

(ii) measurement of the height of the surface step induced by the lift-off of the top layer when part of the incoming Nd:YAG beam is blocked.

Both measurements yield a membrane thickness of 110$\pm$20 nm.

Structural information about the crystallized a-Ge was obtained by Raman backscattering experiments (Fig. 2). The Raman spectrum of the original amorphous film, characterized by a broad structure centered at 270 cm^{-1}, is shown in A. The spectrum obtained after LC of a-Ge [Curve B, corresponding to the TRR measurements of Fig. 1(a)], is dominated by the scattering by optical phonons in microcrystalline Ge;[10] it shows negligible amorphous contribution. The line is slightly asymmetric and redshifted with respect to bulk c-Ge by 1.0$\pm$0.5 cm^{-1}. These effects are attributed to a combination of finite crystallite sizes[11] and stresses,[12] which play an important role in laser crystallized materials.[3] Using a model for the crystallite size dependence of the Raman line similar to that used for silicon,[10,11] we estimated a lower bound of 10 nm for the average crystallite size. The a-Ge:H surface remaining after the removal of the lifted off membrane is also partially crystallized [curve C, sample from Fig. 1(b)]. In this case the effects of crystallization-induced stresses on the Raman line seem to be more important than for the nonhydrogenated samples: the shift of the peak position with respect to that of c-Ge (6.0$\pm$2.0 cm^{-1}) and the

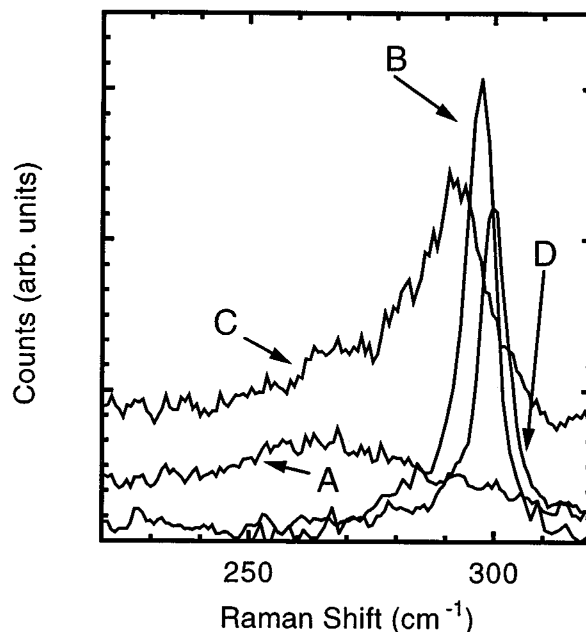
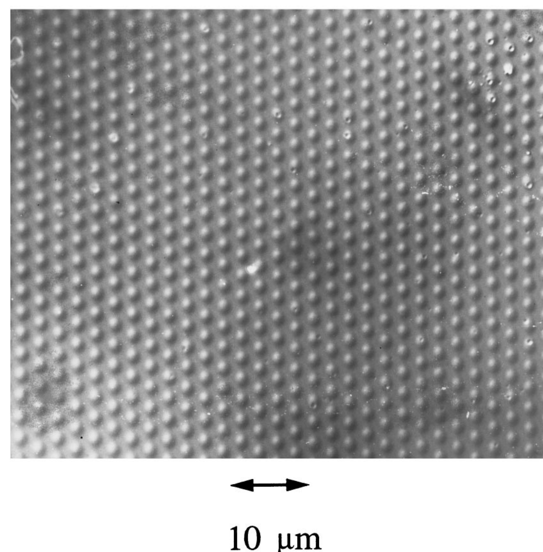


FIG. 2. Raman spectra of germanium samples. Curve A: original a-Ge:H film; curve B: laser crystallized a-Ge [sample of Fig. 1(a)]; curve C: laser crystallized a-Ge:H [sample of Fig. 1(b), after the removal of the lifted-off membrane]; curve D: free-standing Ge membrane.

linewidth (10.0$\pm$4.0 cm^{-1}) cannot be fitted to the calculated parameters for Ge microcrystallites. Grain sizes of less than 5 nm were estimated from the spectra. The Raman spectrum of the lifted off Ge membrane (Fig. 2, curve D) shows a TO peak position and a linewidth which are identical to those of bulk c-Ge [111].

Selective crystallization of a-Ge was achieved by bringing two or three laser beams to interference on the surface of the sample.[2] By appropriate choice of the laser intensity, it is possible to only crystallize the amorphous material close to the interference maxima. Figure 3 shows an optical micro-



10 μm

FIG. 3. Optical micrograph of an hexagonal lattice of crystallized germanium dots (period 2.6 μm) fabricated by three-beam laser interference crystallization.

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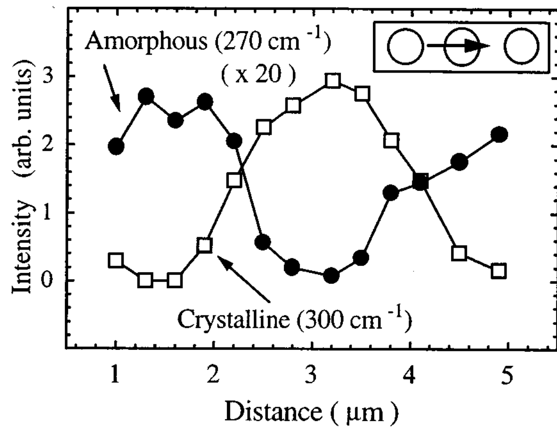

FIG. 4. Spatial variation of the crystalline ($\sim$ 300 cm^{-1}) and of the amorphous ($\sim$270 cm^{-1}) component of the Raman spectrum across a laser crystallized dot of Fig. 3 (see inset). The measurements were performed by micro-Raman spectroscopy with a lateral resolution of 0.7 μm.

graph of an hexagonal lattice of crystallized Ge dots. The incidence angle of the beams was chosen so as to yield a lattice parameter of 2.6 μm. The TRR transient during the LIC of this sample is indicated by LIC in Fig. 1(a). The signal reaches only 35% of the maximum reflection measured in samples crystallized using a single beam (LC). This reduction in signal closely corresponds to the fraction of crystallized area in Fig. 3.

Direct evidence for the crystallinity of the dots is presented in the spatially resolved micro-Raman profiles of Fig. 4. The open squares represent the Raman scattering intensity at $\sim$300 cm^{-1}, corresponding to the maximum in the Raman peak of crystalline Ge, obtained while scanning the probing laser beam across a crystallized dot (see inset). The circles display the corresponding profile at the maximum of the amorphous response at a Raman shift of 270 cm^{-1}. There is a perfect anticorrelation between the amorphous and crystalline signals with the region at the center of (in-between) the dots showing negligible amorphous (crystalline) contribution. The slope of the rising and falling edges of the profiles in Fig. 4 are equal to the lateral resolution of the micro-Raman measurements (0.7 μm), implying that the lateral interfaces between the crystalline dots and their amorphous surrounding are much narrower. Raman spectra obtained on the dots are very similar to those measured on a-Ge crystallized by a single beam (curve B in Fig. 2).

In conclusion, we have demonstrated that good quality crystalline germanium layers with grain sizes exceeding 10 nm can be obtained by single beam short-pulse crystallization of nonhydrogenated a-Ge films. These films can also be used for the fabrication of crystalline germanium structures with submicrometer dimensions using LIC. The laser crystallization of the hydrogenated alloys (a-Ge:H and a-Si:H), on the other hand, is followed by a disruption of the sample surface induced by the presence of hydrogen. This phenomenon can be avoided by annealing using multiple laser pulses.[13]

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[1] J. S. Im and H. J. Kim, Appl. Phys. Lett. **64**, 2303 (1994).
[2] M. Heintze, P. V. Santos, C. E. Nebel, and M. Stutzmann, Appl. Phys. Lett. **64**, 3148 (1994).
[3] D. Toet, B. Koopmans, B. Richards, P.V. Santos and R. Bergmann, *Proceedings of the 23rd ICPS*, edited by M. Scheffer and R. Zimmermann (World Scientific, Singapore, 1996), p. 1123.
[4] C. E. Nebel, B. Dahlheimer, S. Schoniger, and M. Stutzmann, Phys. Status Solidi B **194**, 55 (1996).
[5] J. C. C. Fan, H. J. Zeiger, R. P. Gale, and R. L. Chapman, Appl. Phys. Lett. **36**, 158 (1980); R. L. Chapman, J. C. C. Fan, H. J. Zeiger, and R. P. Gale, *ibid.* **37**, 292 (1980); R. K. Sharma, S. K. Bansal, R. Nath, and G. P. Srivastava, Thin Solid Films **97**, 1 (1982).
[6] C. Cesari, G. Nihoul, J. Marfaing, W. Marine, and B. Mustaftchiev, Surf. Sci. **162**, 724 (1985); D. Kurtze, W. van Saarlos, and J. D. Weeks, Phys. Rev. B **30**, 1398 (1984).
[7] C. J. Fang, K. J. Gruntz, L. Ley, M. Cardona, F. J. Demond, G. Muller, and S. Kalbitzer, J. Non-Cryst. Solids **35/36**, 255 (1980).
[8] R. F. Woods and G. A. Geist, Phys. Rev. B **34**, 2606 (1986); R. F. Wood and G. E. Giles, *ibid.* **23**, 2923 (1981).
[9] O. S. Heavens, *Optical Properties of Thin Solid Films* (Dover, New York, 1991).
[10] J. Gonzalez-Hernandes, G. H. Azarbayejani, R. Tsu, and F. H. Pollak, Appl. Phys. Lett. **47**, 1350 (1985).
[11] I. H. Campbell and P. M. Fauchet, Solid State Commun. **58**, 739 (1986); H. Richter, Z. P. Wang, and L. Ley, *ibid.* **39**, 625 (1981).
[12] E. Anastassakis and E. Liarokapis, J. Appl. Phys. **62**, 3346 (1987).
[13] M. Mulato, O. Toet, G. Aichmayr, P. V. Santos, and I. Chambouleyron (unpublished).

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