Classification
Physics Abstracts
61.40 — 61.50C

Laser induced crystallization of a-Si : H thin films

J. Hajtó, J. Gazsó, G. Zentai and I. Kósa Somogyi

Central Research Institute for Physics, H-1525 Budapest, P.O. Box 49, Hungary

(Reçu le 7 septembre 1981, révisé le 23 novembre, accepté le 4 décembre 1981)

Résumé. — La cristallisation des films amorphes de a-Si : H peut être induite par un faisceau Ar-ion laser continu. La comparaison des résultats de l'expérience avec la résolution de l'équation de la densité de flux thermique montre que le maximum de température au cours de la cristallisation est voisin de 770 °C, considérablement plus bas que le point de fusion du silicium amorphe.

Abstract. — Crystallization in amorphous silicon thin films can be induced by irradiation from a continuous Ar-ion laser. Comparison with the solution of the heat-flow equation shows that the maximum temperature during the crystallization is about 770 °C, well below the melting temperature of the material.

1. **Introduction.** — There is a widespread current interest in laser annealing of silicon thin films and other semiconductor thin films [1-2]. The overwhelming majority of this kind of research is, however, connected with crystalline substances, and laser annealing experiments on originally amorphous films are scarcely mentioned [3]. Dangling bonds present both in the amorphous and in the crystalline states are thought to have detrimental effects on device performance. These dangling bonds arise out of disorder, i.e. throughout the volume of the amorphous phase and at the grain boundaries of the polycrystalline material. It has been realized for some time that hydrogen is efficient in passivating these dangling bonds [4-5].

Preparation of polycrystalline Si films with passivated dangling bonds may be performed through crystallization of hydrogenated amorphous films. It was reported that heat treatment of evaporated a-Si above 600 °C resulted in crystallization [6]. Local heating of the a-Si : H film by appropriate laser irradiation could lead to crystallization, too. The Q-switched laser pulse technique is favoured just because it may be then argued that the crystallization process takes place on a time scale short compared with typical hydrogen diffusion times. We thought that quasi-stationary crystallization (i.e. on a time scale of seconds) induced by a continuous laser though not as efficient as the Q-switched pulse technique still might have advantages over the rather slow conventional heat treatment, where even the much thicker substrate had to be heated up. In our experiments we were able to observe the induced crystal growth under steady state conditions, and to demonstrate convincingly that melting necessitates higher power densities. In addition, we could estimate the maximum temperature during the respective processes from the solution of the heat-flow equation.

2. **Experimentals.** — Amorphous hydrogenated silicon (a-Si : H) films were deposited on fused silica substrates of thickness $d_s = 1.5$ mm, using the now familiar glow discharge decomposition of SiH_4 in a capacitively coupled reaction chamber similar to those described in the literature [7]. The amorphous films referred to in this study were grown to thickness $d = 200$ nm at substrate temperature $T_s = 250$ °C. The chamber atmosphere consisted of 0.5 torr (0.67 mbar) Ar and 0.33 torr (0.44 mbar) SiH_4 , and the rate of the film growth was kept at 0.5 nm/s. Measurements on the optical and the electrical properties indicated parameters comparable to those reported by other laboratories using similar deposition techniques. Figure 1, curve 2 shows the dependence of the absorption coefficient α on the photon energy $h\nu$ in the amorphous state. (The measurements were carried out on a CARY-17D Spectrophotometer.) Curve 3 in figure 1

Fig. 1. — The logarithm of the absorption coefficient α in Si versus photon energy $h\nu$. Curve 1 : single crystal [7]; 2 : amorphous film ; 3 : polycrystalline layer obtained by laser irradiation.

shows the corresponding function for layers crystallized by continuous laser irradiation, the shape of which being very similar to that of curve 1, obtained for single crystal [8]. The one order of magnitude shift upwards is by all probability caused by internal losses on the grain boundaries within the films.

To obtain permanent phase changes induced by irradiation, a cw Ar-ion laser was applied, which could provide four wavelengths : $\lambda = 514.5, 496.5, 488.0$ and 476.5 nanometers, respectively. We were searching for threshold values in the irradiating power densities at which the desired phase transition (crystallization or melting) just started to take place in the duration of sufficiently long times (tens of seconds) after the irradiation had been focussed onto the investigated volume element. The parallel laser beam was focussed into a converging conical beam with the help of a lens of 5 cm focal length. We assume that the radial distribution of the laser beam intensity is of the Gaussian form :

$$I(r) \sim \exp(-r^2/s^2). \quad (1)$$

Hence s will be called the « radius » of the laser beam. In order to facilitate observation a magni-

lying system of lenses was mounted behind the sample, and it projected the enlarged picture of the irradiated spot onto a screen. Thus the resolution power of the system was of the order of $1\text{ }\mu$ (i.e. the features of the projected picture which could be distinguished by the naked eye corresponded to actual sizes of the order of $1\text{ }\mu$). The irradiated spot diameter could be altered easily by displacing the focussing lens relative to the sample.

The first effect to observe was permanent photodarkening, which is supposed to be connected with the exodiffusion of hydrogen (see e.g. [9]). Typical values for the power density are 75 mW on a spot of $40\text{ }\mu$ in diameter. Photodarkening accompanied the crystallization experiments.

Fig. 2. — Photodarkening and crystallization in a-Si : H films.

Figure 2 shows a picture where besides the spots photodarkened only are others which contain crystals in their centre (i.e. the cornered light spots). The typical power density necessary for induced crystallization was found to be about 150 mW on spots of $40\text{ }\mu$ in diameter. It was informative to learn that a definite threshold did exist in each case, to a fairly good degree of reproducibility. We think it important to note that we could not find any sign of the so-called « explosive crystallization » [10]. This effect, if present, would appear spectacularly : as soon as a tiny piece of the amorphous film had been transformed into crystalline state with the help

Fig. 3. — Crystallized strips in Si by the cw laser technique $\lambda = 514.5\text{ nm}$: spot diameter = $120\text{ }\mu$; incident power = 300 mW ; lateral speed = $26\text{ }\mu/\text{s}$.

of the external forces (i.e. with the laser irradiation in our case) then the crystallization front would propagate radially outward spontaneously the driving force being the latent heat of crystallization. In our case we found, on the contrary, that the final size of the crystal depended on the incident power distribution. Relatively large crystals ($\sim 25 \mu$) could be produced by broader spots (Fig. 2). Even extended areas could be transformed into crystalline state by the slow movement of the Si film in its plane. For details, see figure 3.

Next we tried to establish the threshold necessary for melting the crystal already present in the middle of the irradiated spot. It can be achieved by either increasing the incident power or by reducing the diameter of the irradiated spot or by a combination of both. When melting eventually occurs, it must be then the melting point of the crystalline Si which is known to be $1\,410^\circ\text{C}$. We found that the input power had to be sufficiently increased if the spot diameter was kept the same (40μ) : 285 mW was needed for melting as contrasted with the 150 mW for crystallization.

3. Considerations based on solution of the heat-flow equation. — Owing to the stationary nature and the cylindrical symmetry of the problem, in our case the general heat-flow equation reduces to the steady state form :

$$\kappa_i \Delta T(r, z) = - \rho_i(r, z) . \quad (2)$$

Here Δ represents the Laplace-operator in cylindrical coordinates, the index i specifies the medium ($i = 1$ for the amorphous film and $i = 2$ for the substrate). κ_i stands for the thermal conductivity, and ρ_i is the absorbed power density. Since the substrate is transparent,

$$\rho_2 = 0 . \quad (3)$$

It is of great importance that ρ_1 can be factorized :

$$\rho_1(r, z) = \alpha I_0 \cdot \exp(-\alpha z) \cdot \exp(-r^2/s^2) \cdot (1 - R)/\pi s^2 \quad (4)$$

where I_0 is the incident beam power and R is the reflectivity of the semiconductor surface. It can be shown that the contribution of the infinitesimal layer at $(z', z' + dz')$ to the particular solution of the inhomogeneous equation $T_{\text{IH}}^{(1)}$ is of the form [11] :

$$\varphi(r, z, z') dz' = \int_0^\infty k \cdot J_0(kr) \cdot f(k) \cdot e^{-k|z-z'|} dk \cdot dz' \quad (5)$$

where $J_0(kr)$ is the Bessel function of order zero, and

$$f(k) = \frac{\alpha I_0 (1 - R)}{2 \kappa_1 s^2} \int_0^\infty r' \cdot e^{-r'^2/s^2} \cdot J_0(kr') \cdot dr' \quad (6)$$

which, in turn simplifies to :

$$f(k) = \frac{\alpha I_0 (1 - R)}{4 \pi \kappa_1} \exp(-s^2 k^2/4) . \quad (7)$$

Then

$$T_{\text{IH}}^{(1)}(r, z) = \int_0^d \varphi(r, z, z') e^{-\alpha z'} dz' \quad (8)$$

while the general solution to the homogeneous equation is of the form :

$$T_{\text{H}}^{(i)}(r, z) = \int_0^\infty f(k) \cdot J_0(kr) \cdot [a_i e^{kz} + b_i e^{-kz}] dk. \quad (9)$$

The expansion coefficients a_i , b_i are to be found from the appropriate boundary conditions :

$$\frac{\partial}{\partial z} T_{\text{H}}^{(2)}(z = \infty) = 0 \quad (10)$$

$$T_{\text{IH}}^{(1)} + T_{\text{H}}^{(1)} = T_{\text{H}}^{(2)} \quad \text{at } z = d \quad (11)$$

$$\kappa_1 \cdot \frac{\partial}{\partial z} [T_{\text{IH}}^{(1)} + T_{\text{H}}^{(1)}] = \kappa_2 \frac{\partial}{\partial z} T_{\text{H}}^{(2)} \quad \text{at } z = d \quad (12)$$

and

$$\frac{\partial}{\partial z} [T_{\text{IH}}^{(1)} + T_{\text{H}}^{(1)}] = 0 \quad \text{at } z = 0. \quad (13)$$

The neglect in (10) and in (13) of heat-flow by radiation or by the thermal conductance of the ambient air can be justified by their much less magnitude compared to the typical values of κ_1 and κ_2 . In this context we must admit that while there are data published for crystalline silicon, we could not find any for amorphous Si. On the other hand, κ_2 for the fused silica is well studied [12], and there are general arguments [13] that the thermal conductivities of the amorphous substances may not differ too much. Therefore we chose for simplicity

$$\kappa_1 = \kappa_2 = 4 \times 10^{-3} \text{ cal./cm/s.}$$

The reflectivity was regarded as independent of temperature ($R = 0.39$).

Figure 4 shows the maximum temperature increase ΔT_{max} as function of the absorption coefficient computed along these lines, for the particular case of $s = 20 \mu$ and $I_0 = 100 \text{ mW}$.

Fig. 4. — Computed values of the maximum temperature increase in a-Si : H films *versus* logarithm of α . (Thickness $d = 200 \text{ nm}$, spot radius $s = 20 \mu$, input power $I_0 = 100 \text{ mW}$, reflectance $R = 0.39$.)

It is apparent that above $\alpha = 10^5 \text{ cm}^{-1}$ the peak temperature is insensitive to the exact value of α . This corresponds to our experimental findings. It turns out that the maximum temperature in the spot when crystallization sets in is about 770°C . The corresponding values for darkening and for melting are 400°C and 1450°C , respectively. This latter agrees well with $T_{\text{m}} = 1410^{\circ}\text{C}$.

4. **Summary.** — The cw laser annealing can locally produce (i.e. the crystallization remains localized) hydrogenated polycrystalline Si from a-Si : H layers obtained by glow discharge method. Our experimental findings and numerical calculations show that no melting occurs during the cw laser induced crystallization, in good accordance with the previous measurements [6, 15].

The average size of grains is not less than 2 μm and strongly depends on the experimental conditions. There are indications that the grain size can exceed 100 μm as verified by polarized microscope measurements which seems to be promising in view of better photovoltaic conversion efficiency [14] in solar cell applications. It may be noted that, in contrast to the observations on cw laser annealing of rf sputtered a-Si [15], there was no sign of surface deterioration in our samples caused by explosive hydrogen release.

Acknowledgments. — The authors are indebted to Mr. G. Pesti and Mr. L. Takács for their kind assistance.

References

- [1] *Laser and electron beam processing of materials*, edited by C. W. White and P. S. Peercy (Academic Press, New York) 1980.
- [2] ANDREW, R., BANFAY, L., LAUDE, L. D., LOVATO, M. and WAUTELET, M., *J. Physique Colloq.* **41** (1980) C4-71.
- [3] SUSSMAN, R. S., HARRIS, A. J. and OGDEN, R., *J. Non-Cryst. Solids* **35-36** (1980) 249.
- [4] PANKOVE, J. I., LAMPERT, M. A. and TARNG, M. L., *Appl. Phys. Lett.* **32** (1978) 439.
- [5] SEAGER, C. H. and GINLEY, D. S., *Appl. Phys. Lett.* **34** (1979) 337.
- [6] THOMAS, B. A., BRODSKY, M. H., KAPLAN, D. and LEPINE, D., *Phys. Rev. B* **18** (1978) 3059.
- [7] CHITTICK, R. C., ALEXANDER, J. H. and STERLING, H. F., *J. Electrochem. Soc.* **116** (1969) 77.
- [8] DASH, W. C. and NEWMAN, R., *Phys. Rev.* **99** (1955) 1151.
- [9] ZELLEMA, K., GERMAIN, P., SQUELARD, S. and MONGE, J., *J. Non-Cryst. Solids* **35-36** (1980) 225.
- [10] MINEO, A., MATSUDA, A., KUROSU, T. and KIKUCHI, M., *Solid State Commun.* **13** (1973) 329.
- [11] IVANENKO, D. and SOKOLOV, A., *Classical theory of fields* (Moscow) 1951, p. 45.
- [12] *Handbook of thermophysical properties of solid materials*, vol. 3, p. 895, editors : Goldsmith, A., Waterman, T. E. and Hirschhorn, H. J. (Pergamon, Oxford) 1961.
- [13] STEVELS, J. M., *Handbuch der Physik*, Editor : S. Flügge (Springer, Berlin) Vol. 13, 1962, p. 576.
- [14] HOVEL, H. J., *Solar cells (Semiconductor and semimetals)* (Academic Press, N. Y.) 1975, p. 103-109.
- [15] THOMAS, J. P. and FALLAVIER, M., *J. Appl. Phys.* **52(1)** (1981) 476.