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A comparison between furnace and cw laser annealing of a-Si : evidence of different crystallization states

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Résumé. — Deux états de cristallisation du silicium sont obtenus par recuit laser en phase solide du matériau amorphe. La comparaison de ces résultats avec ceux fournis par le recuit thermique, type four, donne des renseignements sur le processus de nucléation-croissance à haute température.

Abstract. — Two states of crystallization of silicon can be obtained by cw laser annealing of amorphous material before melting temperature. Comparison between furnace and cw laser annealing of amorphous films give insights about the nucleation and growth process at high temperatures.

1. Introduction. — The crystallization of thin amorphous silicon films (a-Si) deposited on insulators has been widely studied as its technological advantages are considerable. In furnace annealing (FA), the amorphous-to-crystalline transition occurs near 620 °C [1] and growth of crystallites follows up to 1 425 °C, at which point the liquid phase appears. In cw laser annealing (LA), at low scan speed (< 30 cm/s), two transitions have been found to take place before the liquid phase is reached [2-4]. The existence of a first state of crystallization has been pointed out by Bösch and Lemons [5]. To be reported in the present paper are : (i) the existence of a second state of crystallization prior to the liquid phase ; (ii) the abruptness of this second transition ; (iii) the difference between this second state and the crystallization state obtained by furnace annealing ; and (iv) the relationship between the occurrence of this state and the deposition methods used beforehand.

2. Experimental procedure. — a-Si films, typically 300 nm thick, were deposited at 525 °C on 800 nm oxidized p-type (100) silicon wafers by pyrolysis of pure silane under low pressure (LPCVD). Furnace annealing of the samples was carried out under vacuum for one hour with step increases of 15 °C. Laser annealing was performed using a cw argon laser in the multiline mode, at room temperature and in air. The spot diameter was 60 μm at $1/e^2$, the laser power being increased in steps of 0.2 W between successive test areas. The states of crystallization were characterized by reflexion spectra of films between 900 and 200 nm

using a Beckman DU-8 spectrophotometer and by transmission electron microscopy (TEM).

3. Results and discussion. — The reflexion spectra of (100) monocrystalline silicon, the a-Si/SiO₂/Si starting structure and a poly-Si/SiO₂/Si structure are shown in figure 1. In the 900-500 nm range, interferences due to the multilayer structure (SiO₂ and Si) can be observed (these will not be studied here). In the 500-200 nm range, the reflectivity corresponds to the absorption band for silicon. The extrema near 365 nm (E1) and around 290 nm (E2) correspond to a direct band transition and an absorption maximum, respectively [6]. The shape of spectra below 350 nm depends on crystallite size (in the same order of magnitude as the wavelength), surface roughness and eventually, the presence of a SiO₂ layer which may have grown during annealing [7]. Nevertheless, by comparing the different reflexion spectra of the samples at various stages of crystallization, qualitative information can be obtained concerning the different processes involved.

The characteristic spectra of furnace or laser annealed samples are represented in figure 2. The extrema (E1) and (E2) start to appear in the spectrum of furnace annealed samples at 625 °C while only slight modifications occur at higher annealing temperatures (Fig. 2a). As several investigators have pointed out, this corresponds to the amorphous-to-crystalline transition. Electrical measurements on samples annealed up to 700 °C confirm the occurrence of this transition [8]. Once this transition has taken place, only modifications in the solid phase (increase in grain

Fig. 1. — Reflexion spectra of (a) mono-Si, (b) a-Si/800 nm SiO₂/mono-Si, (c) poly-Si deposited at 630 °C/800 nm SiO₂/mono-Si. The a-Si spectra are independent of the deposition temperature below 575 °C.

size) can be observed [1]. The spectra of samples annealed with a laser power of 0.8 Pm are similar to those of the furnace annealed samples represented in figure 2a within less than 1 %. Pm is the laser power required for local melting of silicon, characterized by the appearance of what is called optical damage (OD) in microscopy.

The spectra of samples annealed using a laser power of 0.95 Pm (Fig. 2b) and Pm (Fig. 2c) are invariably very different from those of FA samples at high temperature, but some similarities to the spectrum of monocrystalline silicon can be observed (Fig. 1a) in the 400-200 nm wavelength range. The increase of reflectivity below 250 nm (Fig. 2c) is at least partly due to the high surface roughness of these samples. This surface roughness is brought about by melting and mass transport and was observed by optical microscopy in the Nomarski mode of laser annealed

Fig. 2. — Reflexion spectra of samples : (a) FA at 655 °C/1 h or LA at 0.85 Pm, (b) LA at 0.95 Pm, (c) LA at Pm.

silicon samples deposited on quartz substrates. The plateau in the 250-200 nm wavelength range (Fig. 2b) and the absence of surface roughness of annealed samples strongly suggest that the crystallization process took place in the solid phase.

For a laser scan speed of 20 cm/s, the range of laser power available (or necessary) to obtain this state of crystallization is 0.2 W. This value is also the resolution of our laser system. The laser scan speed is therefore a critical parameter for below 20 cm/s the resolution of our laser system does not permit the existence of this particular state of crystallization and above 30 cm/s explosive crystallization begins to occur [2, 4].

This narrow range of existence is likewise confirmed by transmission optical microscopy of laser annealed amorphous silicon films deposited on transparent quartz substrates. In this case, we have pointed out [3] that the absorption coefficients of the two states of

crystallization, labelled FCR-1 and FCR-2, are very different and the transition between them is very abrupt.

The steep transitions between the a-Si and FCR-1 zone and also between FCR-1 and FCR-2 observed by optical microscopy are confirmed by TEM micrographs (Fig. 3) of a sample annealed by using a single line laser at 20 cm/s and 0.95 Pm. The FCR-1 diffraction pattern is composed of fine rings which is characteristic of poly-Si and fuzzy halos due to a-Si. The FCR-2 diffraction pattern shows only the fine rings characteristic of poly-Si. The grains grow slowly in FCR-1 until they reach 40 nm, whereas in FCR-2, the typical grain size is 90 nm or larger.

The differences between the crystallization processes occurring in LA and FA are summarized in figure 4. The yield from the crystallization process is time and temperature dependent. But the main difference between FA and LA is the rise time, which is always shorter in LA. The classical nucleation-growth theory explains the FA results. As discussed by Köster [8], when there is a slow temperature rise, first nucleation and then growth takes place. By the time the temperature reaches 630 °C, the a-Si is completely converted into poly-Si and the growth process will carry on until the melting temperature, T_m , is reached. This defines

the solid phase growth associated or not with a secondary crystallization [1, 9]. On the other hand, with a shorter temperature rise time, the nucleation-growth process will differ according to the temperature reached. As laser power increases, the outcome varies in the ways shown in figure 4. At low power (0.8 Pm), the first state of crystallization, FCR-1, is obtained.

In a single line laser anneal, this solid phase is composed of poly-Si and some remaining a-Si. A complete crystallization of silicon can be achieved by subsequent multi scanning or overlapping and the reflexion spectrum of this film is analogous to that of an FA sample shown in figure 2a. At higher laser power (0.95 Pm), one observes a different crystallization process. To our knowledge, the nucleation and growth process of silicon at high temperatures has not yet been investigated. The growth rate of FCR grains, calculated from the grain size (90 nm) and the dwell time, is about 0.18 cm/s; this value is consistent with that obtained from an extrapolation of Köster's results in the high temperature range. Taking this crystallite size, the nucleation rate can be evaluated at 10^{19} nuclei/cm³; this value is in good agreement with that deduced from an extrapolation of data given by Zellama *et al.* [10] at a temperature in the 600°-700 °C range and as well as those given by Köster [9]. In

Fig. 3. — (a) TEM dark field micrograph of half width of a single LA line. (b) blow up of the transition zone between FCR-1 and FCR-2.

Fig. 4. — Schematic of the different process : $t_0 \gg t_1 > t_2$ takes into account the annealing time in FA and LA respectively. The complete crystallized FCR-1 is obtained either by multiple scan or by higher overlap of crystallized lines.

this latter case, however the schematics of the nucleation-growth process has to be revised in the high temperature range ($> 1\,100\text{ }^{\circ}\text{C}$). We feel that the maxima of the nucleation and the growth rate curves are probably situated closer to one another, i.e. at around $1\,200\text{ }^{\circ}\text{C}$. However, we recognize that the validity of this extrapolation on the nucleation rate may be questionable.

The abrupt increase in grain size between FCR-1 and FCR-2 also suggests that, in addition to the gaussian temperature profile induced by the laser spot, another heat source contributes to a threshold temperature. Since the scan speed is 20 cm/s , the temperature rises rapidly and, from the amorphous phase, grains begin to grow. This growth may be due to nuclei either present before laser treatment or formed during heating. The latent heat released during this crystallization increases the local temperature further in a self-enhanced process which appears if the following conditions are simultaneously present :

- (i) the purely laser-induced crystallization involves a significant fraction of the amorphous layer, so that the released heat is sufficient to initiate the self-enhancement ;
- (ii) the released heat does not diffuse away from the layer during laser treatment.

The first condition is clearly met since the FCR-2 crystallization process starts above that of FCR-1 in which state the crystallized fraction is already significant.

As for the second condition mentioned, it can only be explained by one of two possibilities : either each growing crystallite makes use of the latent heat, or it is put to « collective » use on the scale of the layer's thickness. Under our conditions, the dwell time is about $5 \times 10^{-5}\text{ s}$, leading to heat diffusion lengths of $20\text{ }\mu\text{m}$ in silicon ($D_{\text{th}} \sim 0.1\text{ cm}^2/\text{s}$) or $2\text{ }\mu\text{m}$ in silica ($D_{\text{th}} \sim 10^{-3}\text{ cm}^2/\text{s}$). Clearly then, the latent heat can only be used on the scale of the complete layer.

It thus becomes clear that FCR-2 crystallization is strongly dependent on dwell time. For longer times (as in FA), the latent heat will be dissipated without any significant increase in the growth rate, whereas for shorter times, it is completely confined in the Si layer,

leading to explosive phenomena. At scan speeds higher than 30 cm/s and with a laser power of 0.95 Pm , the local and vertical use of the latent heat results in a cooperative movement and generation of a front. Given the amount of heat present, T_{m} can be reached and thus the liquid phase explosive phenomena (LP-XCR in Ref. [2]) occur.

Another mechanism can also be observed at higher scan speed ($> 100\text{ cm/s}$). For such speeds, only FCR-1 occurs (due to the time dependence of FCR-1 and FCR-2[2]). During scanning at 0.8 Pm , the latent heat is also put to use, but in this case, we can only speak of a heat front creating a high rate of nucleation ahead of the laser spot. This results in the so-called Solid Phase Explosive phenomena [2]. Finally, the FCR-2 regime is strongly dependent on the state of the starting material. In our experiments, the best quality FCR-2 was obtained on a-Si films deposited by plasma-CVD as described by Morin *et al.* [11]. The formation of FCR-2 appears less and less clearly depending on whether a-Si is deposited by using LPCVD at low temperatures, vacuum evaporation, sputtering or high frequency plasma-CVD, in that order. In all likelihood, the impurity content of the films plays a key role [12].

In conclusion, we have shown, that the crystallization of a-Si thin films on insulating substrates is associated with a characteristic annealing time. In LA at low scanning speeds, we find the classical process of nucleation-growth to be identical to that found in FA. In addition, and only in the case of laser annealing, at a scan speed near 20 cm/s , a second crystallization process spurred by latent heat occurs. The use of this heat results in the explosive phenomena for scan speeds over 30 cm/s .

This crystallization process is strongly dependent on the state of the starting material, and is observed in a narrow range of laser power, typically 0.95 Pm , whereas the first transition (amorphous to polycrystalline) occurs at 0.8 Pm .

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