

INFLUENCE OF LAYER THICKNESS ON NUCLEATION IN AMORPHOUS SILICON THIN FILMS

S. ROORDA, D. KAMMANN, W.C. SINKE

FOM-Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

G.F.A. VAN DE WALLE and A.A. VAN GORKUM

Philips Research Laboratories, P.O. Box 80.000, 5600 JA Eindhoven, The Netherlands

Received 18 December 1989

Solid phase crystallization in amorphous Si films of different thicknesses is investigated. It is found that the rate (per unit area) at which crystalline grains nucleate increases with the layer thickness. This is a strong indication that nucleation in amorphous Si occurs throughout the volume of the material rather than at the surface.

Classical nucleation theory describes solid state nucleation as a random process which occurs homogeneously throughout the volume of the material under consideration [1,2]. In practice however, nucleation often occurs ("heterogeneously") at interfaces, impurities and/or defects. Only in very clean and sufficiently small systems may one expect to observe homogeneous nucleation [3]. Even then it is hard to prove that the nucleation does indeed occur homogeneously: either the nuclei are too small and too few to be observed, or the nuclei have grown into large entities from which it is no longer possible to determine the exact location where nucleation took place. One system where nucleation may happen homogeneously is that of unseeded solid phase crystallization of thin layers of amorphous silicon (a-Si). In fact, several studies indicate that random crystallization in this system can indeed be described as a homogeneous nucleation process [4-8], although no attempt has been made to separate contributions from volume and interface nucleation. In this Letter, nucleation experiments on a-Si layers of several thicknesses are presented, which makes it possible to distinguish between those two contributions. The results show that the number of nuclei appearing in the film is proportional to the layer thickness. This is an indication that nucleation in a-Si is a homogeneous process.

Ultraclean a-Si layers of 0.2 and 0.4 μm thickness were deposited by e-gun evaporation on thermally oxidized Si wafers. The deposition rate was 0.3 nm/s. The base pressure was 3×10^{-9} Pa, during deposition the pressure rose to 3×10^{-7} Pa, consisting mostly of hydrogen. Before exposure to air, the layers were annealed at 670 K during 30 min in order to densify, preventing in-diffusion of impurities such as water vapour or oxygen. These layers were then annealed in a quartz-tube furnace under flowing dry nitrogen at a temperature of 895 K in order to induce random crystallization. After this anneal, the samples were immersed a few seconds in a Wright-etch mixture [9]. This attacks amorphous material but leaves crystalline Si (c-Si) relatively unaffected. Separate c-Si grains which originated during the thermal treatment thus become visible, provided the (lateral) size of the grain exceeds the thickness of the deposited layer. Grains were observed by scanning electron microscopy (SEM). Some samples were subjected to analysis by X-ray diffraction, which established the presence of crystalline Si. The fraction of crystalline material and the number of crystalline grains were determined from the SEM micrographs as a function of annealing time. In order to determine the fraction of crystalline material, a number of straight lines was drawn *at random* on the micrographs. For every line, the ratio of crystalline-to-

amorphous was determined by measuring the length of the lines in the light and dark regions, respectively.

SEM pictures of annealed-and-etched samples are shown in fig. 1. Figs. 1a and 1b were taken on 0.2 μm film samples and figs. 1c and 1d were taken on 0.4 μm film samples. The annealing times were 91 min for figs. 1a and 1c and 152 min for figs. 1b and 1d. Crystalline grains appear light gray on a dark background. From examination of the pictures shown in this figure, it is evident that the number of grains and the average grain size increase with annealing time, and that the grain density is larger for the samples with the thicker amorphous layer. This can be made quantitative by examination of the crystallized fraction on the micrographs.

The fraction of crystalline material $F(t)$ in an amorphous film of thickness d in which homogeneous nucleation takes place can be expressed as a function of the annealing time t in the Avrami-Mehl-Johnson equation [6,10]:

$$F(t) = 1 - \exp[-(t - t_0)^3 / t_c^3] . \quad (1)$$

In this expression t_0 is the incubation time, which is determined by the mechanism of nucleation and not by the shape or size of the amorphous film. The characteristic crystallization time t_c can be expressed as

$$t_c = (\frac{1}{3}\pi v^2 d I)^{-1/3} , \quad (2)$$

where v represents the growth velocity of a crystalline grain and I the nucleation rate *per unit volume*. It is noted that t_c depends on the film thickness while t_0 is independent of film thickness.

Fig. 2 shows the experimentally determined crystalline fraction as a function of annealing time for both films. Each point represents the average value of 6 micrographs of $\approx 160 \mu\text{m}^2$, randomly distributed over a sample area of $\approx 1 \text{cm}^2$. The variance, as indicated in the figure, is an average value: for very small fractions the variance is somewhat smaller and for large fractions almost twice as large as indicated. Solid circles represent results on 0.2 μm thick sam-

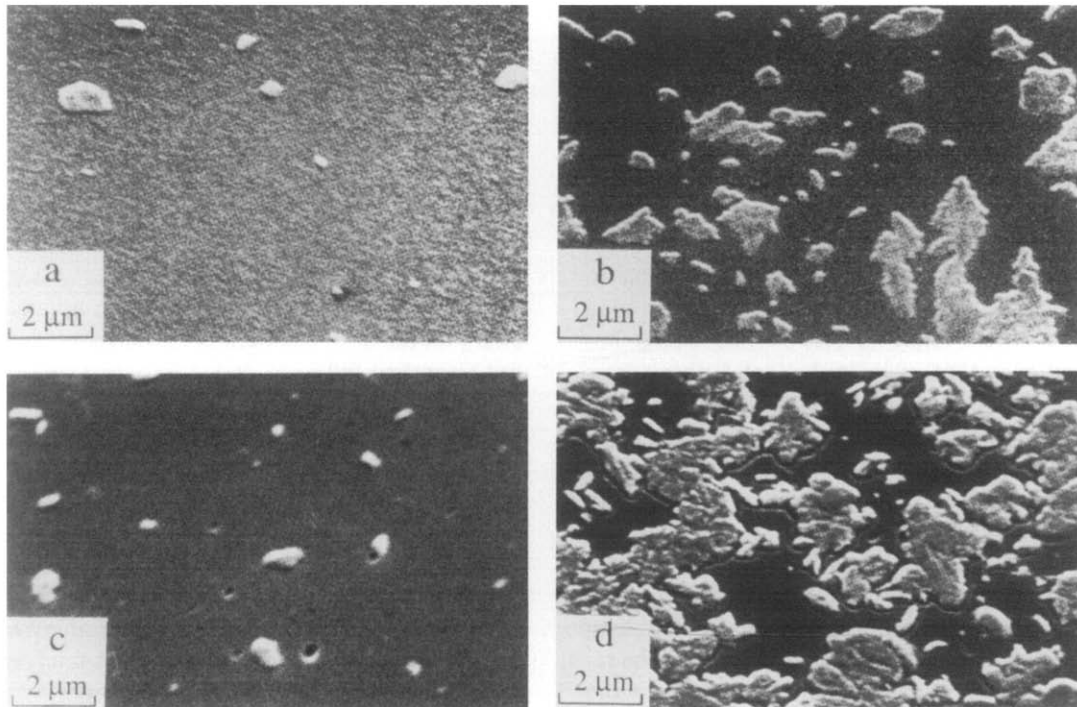


Fig. 1. SEM micrographs of (895 K) annealed and Wright-etched a-Si films. (a) 0.2 μm thick film, anneal time 91 min, (b) 0.2 μm thick film, anneal time 152 min, (c) 0.4 μm thick film, anneal time 91 min and (d) 0.4 μm thick film, anneal time 152 min.

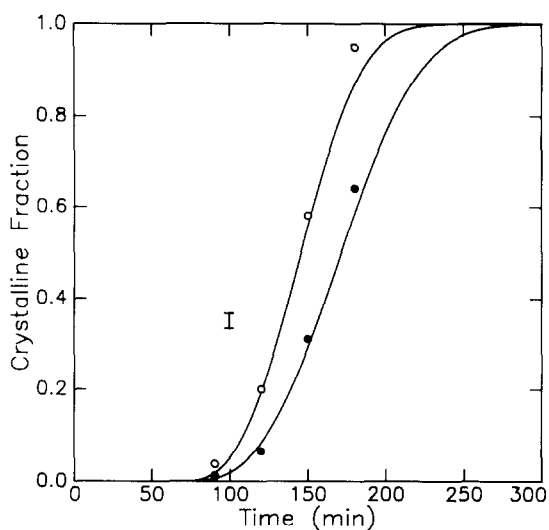


Fig. 2. Crystalline fraction as a function of anneal time. Solid circles: 0.2 μm thick films; open circles: 0.4 μm thick films. Curves: fits to the data (see text).

ples and open circles represent results on 0.4 μm thick samples. It can be observed immediately that there is a large transient time of more than 1 h before crystallization occurs, indicating that the deposited films are free of crystal seeds. The curves in the figure are best fits of the Avrami-Mehl-Johnson equation (1) to the data points. The obtained fits describe the data reasonably well. The parameters t_0 and t_c obtained from these fits are shown in table 1. It is observed that t_c is substantially smaller for the thicker film, while t_0 is equal for both film thicknesses. This is a strong indication that nucleation occurs homogeneously throughout the volume of the samples rather than at the surface or at the interface with the underlying substrate. A quantitative test is to compare the actual ratio of the layer thicknesses with an estimate of this ratio from the characteristic times; it

Table 1
Parameters (and variance) obtained from fits in fig. 2

Film thickness (μm)	t_0 (min)	Δt_0 (min)	t_c (min)	Δt_c (min)
0.2	68	5	117	7
0.4	66	3	90	4

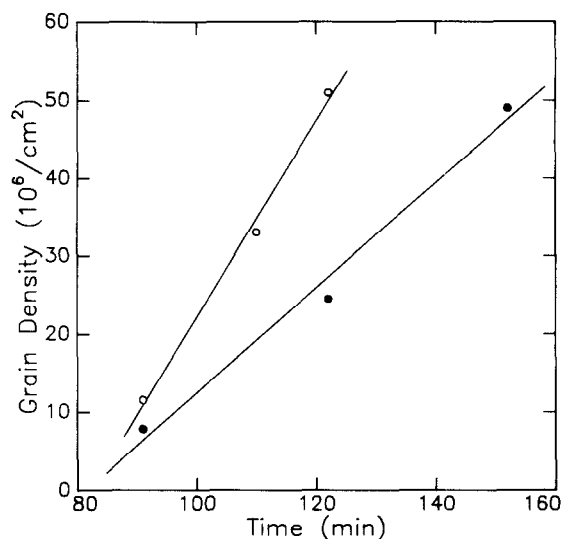


Fig. 3. Grain density as a function of anneal time. Solid circles: 0.2 μm thick films; open circles: 0.4 μm thick films. The lines are least-squares fits to the data.

can be estimated by $[t_c(0.2 \mu\text{m})/t_c(0.4 \mu\text{m})]^3$. This gives a ratio of 2.2, which is close to the actual ratio $0.4/0.2=2$, as determined by Rutherford backscattering spectrometry. This confirms the above conclusion that nucleation is a volume rather than a surface process.

The areal density of grains as a function of annealing time is shown in fig. 3. The density has been corrected to account for the fact that the amount of available amorphous material decreases as crystallization proceeds. The lines are least-squares linear fits to the data. The slope of the fits can be identified as the nucleation rate. The nucleation rate is found to increase from $0.68 \times 10^6 \text{ cm}^{-2} \text{ min}^{-1}$ for the 0.2 μm thick film samples to $1.3 \times 10^6 \text{ cm}^{-2} \text{ min}^{-1}$ for the 0.4 μm thick film samples. Thus the nucleation rate *per unit area* is found to increase with the thickness of the film. The ratio of the nucleation rates is 1.9, which is very close to the ratio of the layer thicknesses. This indicates that nucleation of crystalline grains occurred predominantly throughout the volume of the a-Si layer rather than at the interface and free surface of the film. The *volume* nucleation rate at 895 K is thus found to be $5.4 \times 10^8 \text{ cm}^{-3} \text{ s}^{-1}$, which is in good agreement with other results [4-6]. From this nucleation rate, together with the values for t_c as

determined from the fits in fig. 2, the grain growth velocity v can be determined using expression (2). It is found that v equals 1.6–1.7 Å/s, which may be compared with the slow $\langle 111 \rangle$ regrowth rate during solid phase epitaxial regrowth (at the same temperature) according to Csepregi et al. [11] of 1.3 Å/s.

Although the results are strongly suggestive of homogeneous nucleation, other mechanisms have to be considered which cannot be ruled out completely. It is conceivable that nucleation in a film occurs only at the interface between a-Si and the underlying oxide. Supposing that the nucleation rate depends on the strain at this interface and that this strain increases as the thickness of the deposited layer is increased, it is possible to construct an alternative explanation of the results presented. A second mechanism could be that nucleation occurs at the free surface of the deposited film. If the nucleation rate is dependent on surface roughness and if this roughness increases as the thickness of the deposited layer is increased, then this mechanism would lead to the behaviour as observed. However, it is not very likely that in these scenarios the incubation time is the same for both film thicknesses as is observed in this work.

In summary, it has been shown that unseeded crystallization of a-Si thin films depends on the thickness of the film. Crystallization can be characterized by a thickness-independent incubation time and a characteristic time which decreases as the film

becomes thicker. In addition, the number of nuclei that appear in the films under certain anneal conditions, increases with film thickness. Both observations indicate that unseeded crystallization in a-Si is mediated by homogeneous nucleation rather than by a surface or interface related nucleation process.

This work was supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) and the Stichting Technische Wetenschappen (STW).

References

- [1] M. Volmer and A. Weber, *Z. Physik. Chem.* 119 (1926) 277.
- [2] K.F. Kelton, A.L. Greer and C.V. Thompson, *J. Chem. Phys.* 79 (1983) 6261.
- [3] D. Turnbull, *J. Appl. Phys.* 21 (1955) 1022.
- [4] U. Köster, *Phys. Stat. Sol. a* 48 (1978) 313.
- [5] K. Zellama, P. Germain, S. Squelard, J.C. Bourgoin and P.A. Thomas, *J. Appl. Phys.* 50 (1979) 6995.
- [6] R.B. Iverson and R. Reif, *J. Appl. Phys.* 62 (1987) 1675.
- [7] R.B. Iverson and R. Reif, *Mater. Letters* 5 (1987) 393.
- [8] S. Roorda and W.C. Sinke, *Appl. Surface Sci.* 36 (1989) 588.
- [9] M. Wright Jenkins, *J. Electrochem. Soc.* 124 (1977) 757.
- [10] M. Avrami, *J. Chem. Phys.* 8 (1940) 212.
- [11] L. Csepregi, E.F. Kennedy, J.W. Mayer and T.W. Sigmon, *J. Appl. Phys.* 49 (1978) 3906.