

Phenomenology of the "explosive" crystallization of sputtered non-crystalline germanium films

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Certain non-crystalline germanium films ($> 10 \mu\text{m}$ in thickness) prepared by rf-sputtering crystallize "explosively" at room temperature when initiated by pricking the surface with a sharp point (or certain other methods). The propagation velocity of the crystallization at room temperature was found to be as fast as 1200 mm sec^{-1} depending somewhat on the conditions of film preparation, thickness, etc. The density of several such crystallizable films was determined as $5.05 \text{ g cm}^{-3} \pm 1\%$. The crystallite size in the crystallized films, measured by X-ray broadening, was typically larger than 500 \AA . A model for the crystallization process invokes a cascade energy transfer process, basically thermal in nature.

1. Introduction

Although much work has been reported on non-crystalline germanium films, the thickness of films studied in the literature has rarely exceeded $30 \mu\text{m}$. In the case of films prepared by rf-sputtering, thick films, if needed, can be formed simply by keeping the apparatus running longer. Some films obtained in this way have been found to reveal an interesting and quite unusual crystallization behaviour [1]. The basic facts are as follows.

When a non-crystalline germanium thick film, $50 \mu\text{m}$ thick is deposited on a glass microslide by this technique in an argon atmosphere of 30×10^{-3} Torr, and is pricked or scratched with a knife at room temperature, a part of the film within a sharply defined circular perimeter crystallizes "instantaneously". The crystallization usually results in flaking off of much of the material with occasional cracking of the substrate glass. This "explosive" crystallization of non-crystalline germanium thick films has been demonstrated elsewhere [2]. Because of (1) this (qualitatively) rapid velocity of crystallization propagation, (2) the wavy marks which appeared on the surface of the crystallized films, and (3) the fact that this crystallization "wave" can be damped by a rubber band or even by some

liquids, the authors assumed, at first, that the crystallization "wave" might be transmitted acoustically [1].

The present work was aimed at studying in greater detail, and understanding the mechanism and kinetics of, this anomalous phenomenon of extremely rapid crystallization at room temperature.

2. Experimental procedure

The experimental conditions of sample preparation in the present study were similar to those described in the previous work [1], and further details are described elsewhere [3].

The crystallization of the film could be recognized by the change of the colour from shiny black to metallic gray, and this was routinely confirmed by X-ray diffraction as shown in Fig. 1. To determine the velocity of the crystallization propagation of several films sputtered on glass microslides, a 16 mm high-speed movie camera (Photo-Sonic) was used with a neon timing light for monitoring the speed of the process [4]. The maximum speed of the movie film obtained was $1920 \text{ frames sec}^{-1}$. The thickness of the germanium films was approximately $45 \mu\text{m}$. For further observations on the crystallization process some DTA work

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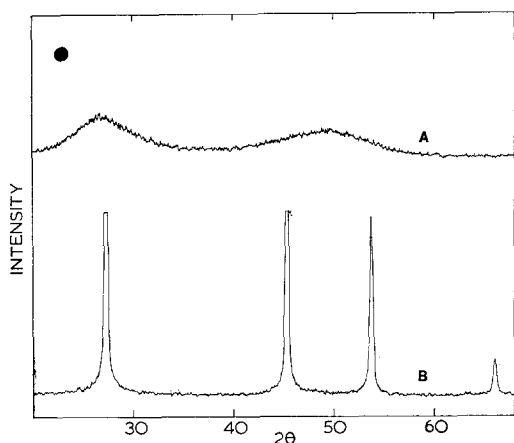


Figure 1 X-ray diffraction patterns (A) before and (B) after the "instantaneous" crystallization of non-crystalline germanium thick films. See text.

and electrical resistance versus temperature measurements were also conducted.

The density of such non-crystalline films was measured to search for a cause for this anomaly. To eliminate most of the errors which may be introduced only because of the thinness of the films, a very thick film (up to 370 μm) was prepared for measurement by the conventional Archimedes method (in both water and carbon tetrachloride) at room temperature.

The surfaces of the crystallized film were examined by replica electron microscopy. Since the crystallization is so "explosive" that the crystallized film in most cases peeled off from the substrate, only the small portions of the film remaining occasionally on the substrate after the crystallization made the replication possible.

The crystallite size of the crystallized film was determined from X-ray line broadening. For the correction for $K\alpha$ -doublet broadening and for instrumental broadening, the procedures of Klug and Alexander [5] were followed. The strongest forward reflection (111) was used to get a better signal to noise ratio sacrificing the sensitivity to crystallite size to some extent. The (111) reflection of silicon and the (101) reflection of α -quartz (both are crushed single crystals) were used as internal standards. Because a low precision could be expected for this method [5], more than six repetitions of the procedure were made for each specimen, and more than three specimens were used for every condition.

Other supplemental experiments are described with the results in the next section.

3. Results

3.1. Velocity of propagation of crystallization

Contrary to the previous assumption that the propagation may be acoustic [1], the propagation event occupied more than 50 frames of the film indicating a propagation velocity too low to be acoustic.

By projecting each of these frames on a screen, successive propagation fronts were sketched. Fig. 2 shows two of these sketches with the propagation front of every fifth frame drawn with a thicker curve to make the profile more obvious. Just after the triggering of the crystallization the propagation is very chaotic, as can be seen in the figure, and then this chaos gradually becomes a circular propagation front which proceeds to the edge of the sharply defined circular perimeter. Approaching this perimeter, the propagation slows down and stops. As was mentioned previously [1], the centre of the crystallizable circular area corresponds to the point directly beneath the centre of the sputtering target, and the radius of the circular area varies with the film thickness and the conditions of preparation, such as the rf-power density and argon gas pressure for sputtering [3]. Along the dashed lines in Fig. 2, the distance versus time relations have been plotted, and a graphical differentiation was attempted for the velocity versus distance relation, which resulted in Fig. 3. In this figure, some examples of the crystallization velocity of the films prepared under the same conditions, but triggered by different methods (pricking and microtorch) and of those prepared by different conditions are compared. Apparently, the velocity of the "steady state" propagation (after the initial chaos) varies by a factor of more than $\frac{2}{3}$, and it seems to depend more on the films, either their preparation condition or thickness, than the triggering mechanism. In Fig. 3, the highest velocity of approximately 1200 mm sec^{-1} was attained. It seems likely that an even higher velocity of propagation is possible with different conditions of film preparation [3]. In every case in Fig. 3, however, it is a consistent trend that after the initial chaotic propagation the rate remains steady over most of the range and finally slows down to a stop.

3.2. Crystallization of substrate-free film

During the preparation of the germanium thick

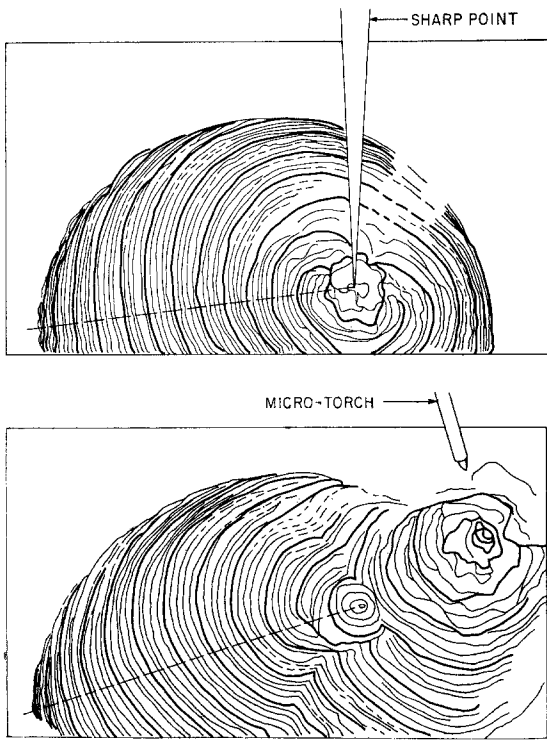


Figure 2 Profiles of the propagation fronts of the crystallization of amorphous Ge triggered (A) by pricking with an “X-acto” knife and (B) by a microtorch. The dashed lines show how the distance versus time relations were taken. The length of the microslide was 46 mm.

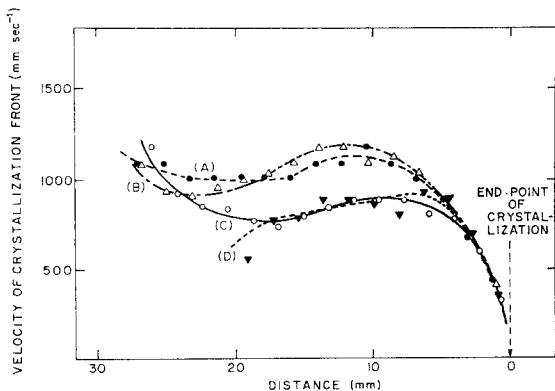


Figure 3 Velocity of propagation versus distance, derived from Fig. 2. Triggers of the crystallization were (A) and (C) pricking with a sharp point (X-acto knife), (B) microtorch and (D) ruby laser pulse. The Ge thick films for both (A) and (B) were prepared under the same condition, which was different from those of (C) and (D).

films under certain sputtering conditions, a tensile stress between the substrate and the film was built up and resulted in portions of the

film peeling from the glass. When a portion of this particular film still remaining attached to the substrate was pricked, the crystallization proceeded into the portion of the film which had peeled. If the whole film (prepared under any sputtering condition) was removed from the substrate by an HF etch [1, 6] however, it could not be crystallized by pricking; even after the film was mechanically pulverized in a mortar the material remained non-crystalline. It was confirmed by several different films, however, that a ruby laser pulse can trigger the propagation of the crystallization similarly even in such substrate-free films.

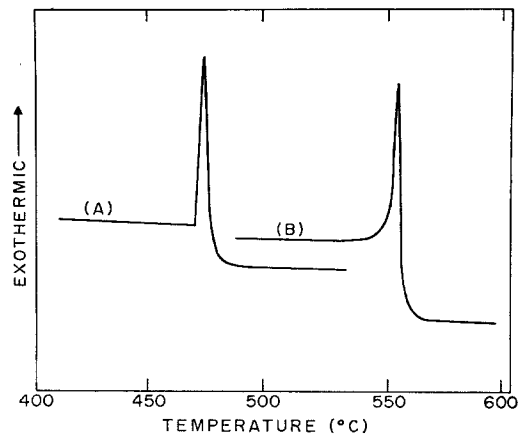


Figure 4 DTA thermograms of the non-crystalline Ge films prepared in 20×10^{-3} Torr argon atmosphere with rf power density 3.3 W cm^{-2} . Sample shapes were (A) granular pieces, and (B) fine powder. In both cases, baseline shifts after the exothermic crystallization were caused by partial loss of sample.

Fig. 4 shows the differential thermal analysis of the crystallization behaviour of the substrate-free films. Curve A, the thermogram of the film, crushed to granular pieces but not to a fine powder, shows a very sharp onset of crystallization at about 470°C . In addition, the rapid reaction caused part of the DTA sample to pop out of the sample container. The crystallization peak of the finely-pulverized sample, curve B, shifted upwards by more than 80°C in this example, in addition to showing a more gradual onset of crystallization. When this pulverized sample was diluted by the addition of 50 vol % Al_2O_3 powder, the crystallization temperature shifted to an even higher value and the “popping out” of the sample was not observed any more.

3.3. Crystallization of films attached to substrates

The crystallization behaviour of similar films to those in the previous section but still attached to the glass substrates was also examined by electrical resistance versus temperature measurements. The "explosive" crystallization in this case was noticed by a sudden open circuit with an accompanying flaking off of the crystallized film from the substrate. The temperature at which this occurred appeared to be a little higher than that on the DTA thermogram for the substrate-free film as shown in Fig. 4, curve A.

3.4. Temperature rise on crystallization

Some qualitative but significant evidence has been accumulated on the large, instantaneous generation of heat on crystallization of the non-crystalline germanium films in the present study. Since the possible temperature attained is important in postulating a mechanism of crystallization, some experiences are enumerated in the following.

1. A thin plastic tape (Scotch No. 74) sticking to the germanium film melted and crumpled when the film was crystallized by pricking "at room temperature".

2. Some attempts were made to crystallize such non-crystalline germanium films at liquid nitrogen temperature, but no trace of crystalliza-

tion was observed even if the films were pricked and scratched very strongly.

3. When one of the authors deliberately touched a thicker film with his bare finger, and crystallized it by pricking, he got a blister burn on the finger.

These crude measures only established that a bulk temperature of at least 200°C was attained. A more quantitative measurement of this instantaneous temperature rise (probably of the order of a microsecond) is now in progress in this laboratory.

3.5. Density of non-crystalline films

The density of "amorphous" germanium has been reported in several recent articles [7-15]. As listed in Table I, the values are scattered from 3.9 to 5.40. If most of these results are accurate within the error limits claimed by the authors of the respective data, the major differences among them must be attributed to the difference in their preparation procedures. Indeed, this single set of data should establish beyond any doubt that there is a wide spectrum of "amorphous" germanium phases with substantially different structures [3, 6, 16]. The anomalous crystallization behaviour of our germanium thick films suggested that their density may be anomalously high or low and attempts were, therefore, made to correlate the behaviour with

TABLE I Comparison of density data in the literature

Method of preparation	Dep. rate (Å sec ⁻¹)	Substrate	Max. thickness (μm)	Method of measurement	Density	Reference
Elec. beam evap.	—	Glass and fused silica	1 ~ 3	X-ray linear absorption coeff.	5.35(± 5%)	7, 8
Elec. beam evap.	3	Pyrex & LiF	23	Picnometry (?) Dow Corning No. 704 Silicone oil	3.9 ± 0.4	9
Elec. beam evap.	10~50	Al foil	1 0.25 1	Geometry and weight	4.54 ± 0.14 4.73 ± 0.05	10 11
Elec. beam evap.	—	Quartz	0.35	Geometry and weight	4.1 ~ 4.2 5.40 ± 0.15	12
Electrodeless rf-glow discharge in germane	2~12	Glass	30	Geometry and weight	4.6 ± 0.2	13
Thermal evap.	10	Glass, mica & rocksalt	2	Geometry and weight	4.7 ± 0.2	14
Sputtered	—	—	11	X-ray total reflection	4.90 ± 0.15	15
rf-sputtering 30 × 10 ⁻³ Torr argon	6	Glass	370	Archimedes method	5.05 ± 0.05	This study

measured densities.

The densities of the crystallizable phases typically obtained were, however, within $\pm 1\%$ at 5.05 g cm^{-3} , which is near the average of the literature data (Table I). (In work completed very recently, Messier *et al* [3] have shown that, in fact, by controlling the sputtering conditions one can control the density of non-crystalline Ge obtained, and that when these densities exceed those of crystalline Ge, the films can no longer be crystallized by scratching.)

3.6. Microscopic and macroscopic observation of crystallized films

Replica electron micrographs of the crystallized films reveal several irregular features and what appeared to be independent “crystallites” over the entire surface in all cases. An example is shown in Fig. 5. Another interesting observation encountered in the course of this work is shown in Fig. 6, which shows a portion of the film remaining on the substrate after the “explosive” crystallization. In the figure, it is observed that the substrate-side layer of the film remained non-crystalline even after the crystallization propagated over the surface of the upper half layer of the film. This was observed only at the portion close to the perimeter of the circle of the crystallization, where the velocity of the crystallization front has slowed down and might easily be suppressed.

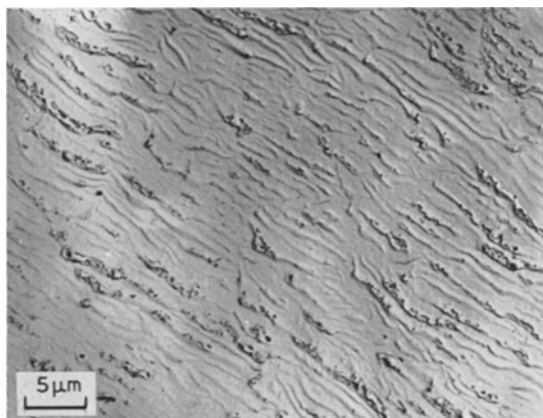


Figure 5 Replica electron micrograph of the surface of the crystallized film $45 \mu\text{m}$ thick. The film was prepared under the condition similar to [1] (30×10^{-3} Torr argon, 3.3 W cm^{-2}).

3.7. Crystallite size of crystallized films

In most cases the crystallite size in crystallized

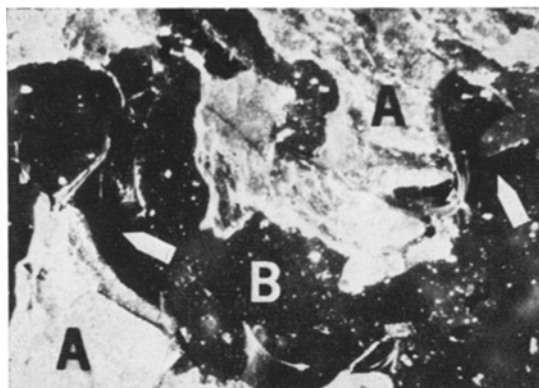


Figure 6 Ge film remaining on the glass substrate after the “explosive” crystallization. Area A shows crystallized Ge and Area B glass substrate. Black areas with a feature of conchoidal fracture (indicated by arrows) show non-crystalline portion of Ge on the substrate side. (Conditions of the film preparation: 5×10^{-3} Torr argon, 3.3 W cm^{-2} , $45 \mu\text{m}$ thick.)

films as measured by X-ray line broadening was found to be larger than 500 \AA . With films of approximately the same thickness, it appears that the final crystallite size is almost exclusively dependent on the preparation conditions of the film, especially on the argon pressure during sputtering. In Table II, some of the crystallite size data obtained from two different conditions of crystallization are compared for films of nearly the same thickness. Of the films prepared under the same sputtering conditions, one film on the substrate was crystallized by pricking, and another film was removed from the substrate by a HF etch and crystallized by laser pulse triggering as mentioned in Section 3.2. In the Table there is no significant difference in crystallite size between these two conditions of crystallization. In contrast, when the argon pressure during the rf-sputtering deposition was

TABLE II Scatter of crystallite size for $50 \mu\text{m}$ films

Argon pressure of sputtering (Torr)	Condition of crystallization	
	Film with substrate, pricked (\AA)	Substrate-free film, laser triggered (\AA)
30×10^{-3}	1300	1160
	1270	1120
	1290	1140
10×10^{-3}	600	540
	610	520
	570	530
	570	

varied from 30×10^{-3} to 10×10^{-3} Torr, the crystallite size of the crystallized films decreased by more than 50%. The reason for this difference of the crystallite size for the films of the same thickness is not yet clear, although it appears to be related to the extent of argon inclusions, which has been shown to be reciprocally dependent to the argon pressure of sputtering [3, 17].

If the thickness is not the same among the films prepared under otherwise identical conditions, it seems that the thicker the non-crystalline film is, the larger is the crystallite size obtained after its crystallization. Further, crystallites in the crystallized films were found to have no significant preferred orientation. This may not be an unexpected result considering the fact that the reaction proceeds only when the thickness of the film is at least on the order of tens of μm , which is two orders of magnitude larger than the crystallite size measured in the above.

4. Discussion

4.1. Velocity of crystallization

The propagation velocity of crystallization obtained above may be best compared to the lock-on speed of memory switching devices [18], which is one of the most rapid crystallizations in solids known currently, has been estimated as about 10 mm sec^{-1} . This is still two orders slower than the result obtained in this work. The size of the germanium crystallites formed by such crystallizations was determined as being greater than 500 \AA . Taking 1000 mm sec^{-1} as a typical velocity of propagation, it is found that a crystallite of 500 \AA forms in $0.05 \mu\text{sec}$. Previously [1], the authors observed concentric wavy marks on the crystallized film by an optical microscope of lower magnification and attributed it to "acoustic" propagation. If such is the case, the average wavelength may be considered to be approximately $0.5 \mu\text{m}$ from Fig. 5. Using the velocity in Fig. 3, however, the frequency in this case is estimated to be only of the order to 10^6 Hz , and, at this frequency, even the maximum velocity in Fig. 3 is too low to be acoustic by a factor of about three orders of magnitude [19]. It is clear, therefore, that the wavy marks which appeared on the film are the result of the crumpling of the film by the stress caused during the crystallization reaction. The marks observed are actually artifacts of the crystallization front.

4.2. Role of the substrate

We have reported previously that the "explosive" crystallization of the germanium thick film could be observed on any of the substrates tried (such as various glasses, fused silica, single crystal quartz, rutile, and α -alumina), and also could be triggered either by a sharp point, a microtorch, an electron beam, or a ruby-laser pulse [1]. As mentioned in Section 3.2, the films even when detached from their substrates are crystallized "explosively" once triggered by suitable means. In addition, subsequent experiments with different sputtering conditions [3] showed that crystallization occurs by pricking with either tensile or compressive stress between the film and the substrate (although the appearance of the crystallized film is slightly different). These facts indicate that the contribution of the strain energy between the film and the substrate is not as important as once assumed [1]. The differences in temperatures attained in the crystallization "explosion" for films both on and off substrates may possibly be owing to the suppression of the crystallization reaction by the substrate, resulting in the shift to the higher temperature. Such a suppression seems consistent with an observation in Fig. 6. The damping of the propagation by a rubber band observed previously [1] is probably the same suppression of the atomic rearrangement as observed here. The reason why the substrate-free film cannot be crystallized by pricking may be simply because of the inability to concentrate enough energy to overcome the barrier for crystallization since the film breaks easily when pricked with a knife. It is understandable that the crystallite size after the crystallization of the films either with or without the substrate remains the same.

4.3. A model for the crystallization process

One model for the unique crystallization process invokes a cascade type energy transfer [1]: i.e., once the activation energy for crystallization is overcome at some portion of the sample by the triggering energy (such as the laser kT , the strain energy when it is pricked, etc), the crystallization of that portion generates a comparatively large amount of energy, which is used to pump the activation energy of crystallization of the next "layer" and so on. The possible energetics of such a process is schematically depicted in Fig. 7. Although it was assumed previously [1] that this condition may be caused by the strain between the film and the substrate, the present results

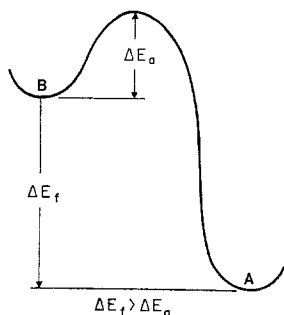


Figure 7 Schematic representation of energy states: A, crystalline state; B, non-crystalline state, ΔE_a , activation energy for transition from B to A. The necessary condition for the maintenance of the cascade reaction is $\Delta E_f > \Delta E_a$. The amount by which ΔE_f must exceed ΔE_a will be determined by the energy coupling efficiency during cascade.

clearly establish that the strain is *not* always necessary. The free energy of the non-crystalline thick film (even in the "substrate-free" condition) is high enough that the energy difference between this state and the crystalline state is sufficient.

It is reasonable to assume that, when the energy coupling efficiency in such a cascade reaction is decreased by any means, an additional thermal energy will become necessary to overcome the activation energy of crystallization and thus to maintain the reaction. The energy coupling efficiency of the sample in a powder form is apparently lower than in a bulk form since the contact between "layers" is much less in the former. The series of DTA results described in Section 3.2 support this argument.

If the crystallization were controlled by the familiar nucleation and growth mechanism, the crystallization peak for the fine powder could never appear at a higher temperature than for bulk material, since the pulverizing procedure would certainly introduce a large number of nucleation sites in the sample. The thermograms in Fig. 4 contrast dramatically with the usual case of the surface-nucleated crystallization, in which the crystallization peak of the sample shifts to lower temperature when the sample is pulverized [20], owing to the increased nucleation sites on the surface.

4.4. Comparison with the martensitic transformation

At first glance, one might be tempted to compare the "explosive" or exceptionally rapid crystallization at room temperature observed in the

present work with the burst phenomena in martensitic transformations. There is little similarity beyond the speed, however. First, a typical martensitic transformation is quite sensitive to the temperature, second (in most cases), the amount of transformation is fixed by the temperature alone [21], while the phenomenon described here occurs either at room temperature (by pricking, etc.) or at temperatures higher than 450°C (by thermal excitation). What the burst phenomena in the martensitic transformations [22] may have in common with the "explosive" crystallization here is the "co-operative" nature of the burst which may be, in fact, a result of the cascade-type energy transfer. Yet all the burst phenomena observed as martensitic transformations occur during cooling whereas the "explosive" nature observed in this study is during heating. Further, for the martensitic transformation the same sample can be repeatedly recycled in the solid state although hysteresis on heat cycling is common [21]. In contrast, the "explosive" crystallization of the non-crystalline germanium film is completely irreversible in the solid state.

Argon or any other gases, included in the film during the preparation procedure [17] appears to be connected to the cause of the "explosive" crystallization phenomenon. The electron microprobe analysis showed [3], however, that there is no significant change in argon content in the film by such a crystallization. Even when the film is crystallized in liquids, observation of bubble formation is rare.

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