Phase Separation by Coupled Single-Crystal Growth and Polycrystalline Fingering in Al-Ge: Experiment

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We describe a new mode of phase separation during the annealing of amorphous Al-Ge alloys. This process is characterized by growth of circular colonies, linear in time at fixed temperature, and with an activated growth velocity. The colonies consist of a branching Ge polycrystalline core and of a nearly monocrystalline Al outer rim, with deep fjords extending into the interior of the colony. The spatial distribution is characterized by a length scale, roughly equal to the thickness of the Al rim, that decays exponentially as the temperature is increased. The measured length scale and growth velocity appear to be consistent with growth controlled by diffusion of Ge atoms from the Al-Ge matrix through the Al rim.

We describe in this Letter the main features of a new mode of phase separation which we have found to occur during the annealing of amorphous Al-Ge alloy thin films.[1] The phase separation results in the growth of colonies that contain both constituents in their crystalline form, the colonies growing at the expense of the surrounding amorphous matrix. The colonies present a remarkable structure, which has been called the dense branching morphology.[2] In this Letter we present detailed data on this structure and its growth dynamics. These new results lend strong support to the theory exposed in the accompanying Letter,[3] which emphasizes the role played by an Al rim (or membrane) that surrounds the colony, and through which Ge atoms must diffuse to produce further growth of the inner crystallized Ge core.

The amorphous Al-Ge films are prepared by vacuum coevaporation of the constituents onto microscope slides previously covered with a soluble material (photoresist). After dissolution of the photoresist, the films are placed on grids (copper or nickel) for observation in the transmission electron microscope (TEM, Philips model EM300) used in the experiment. The Al-Ge films are about 500 Å thick, a typical composition being $Al_{0.4}Ge_{0.6}$. During deposition, the substrates are held at or near room temperature.

It is known that for Ge concentrations larger than 0.45 and substrate temperatures lower than 160 °C, such films are amorphous.[4] At lower Ge concentrations the films obtained at room temperature have the well-known granular structure in which the Al is in the form of small (less than 100 Å) crystallites with a thin Ge amorphous coating surrounding them, the Ge atoms having presumably been expelled from the regions where Al crystallites have nucleated and grown during film deposition. The existence of the granular structure shows that Al nucleates preferentially to Ge, and that the surface tension between Al and Ge must be weak (otherwise the small Ge-coated Al grains would not be stable). Both features will turn out to be important for the understanding of the structure of the colonies.

After preparation, the microscope grid is placed on the heating stage of the microscope, which allows direct observation of the sample during annealing. A typical colony is shown in Fig. 1. It has been grown at a temperature of about 200 °C. The dark areas are mostly composed of Ge crystallites, and the white ones of Al.
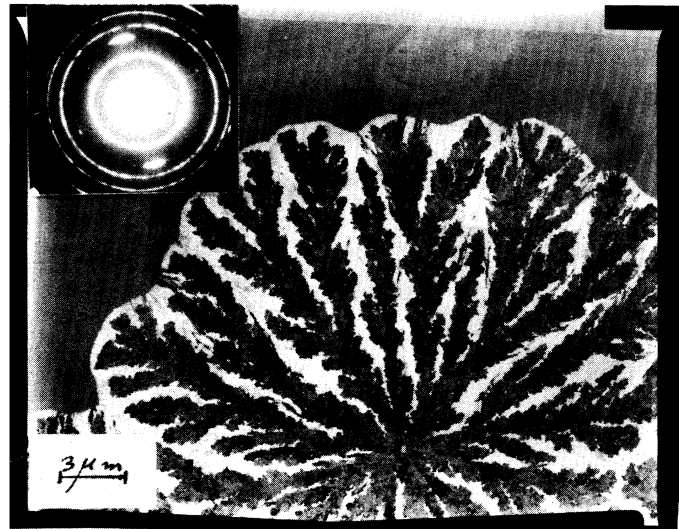

FIG. 1. Typical Al-Ge colony in the steady-state growth regime. Note the clear Al rim and the darker Ge branched core. The grey area beyond the colony's edge is the amorphous Al-Ge matrix. The impression that the Ge core is connected to the amorphous phase in several places is due to diffraction of the Al, whose local orientation obeys the Bragg condition. Inset: Diffraction pattern over a large fraction of the colony. The continuous rings are diffracted from the Ge core (polycrystalline), while the short arcs are due to Al (nearly single crystal).

The colony appears surrounded by a continuous Al rim, several thousand angstroms wide. The core of the colony is composed of a centered and branched Ge structure, whose interstices are filled with Al fjords. This morphology presents some resemblance with that of viscous fingers, as if the Ge had been "injected" from the center.[2] It indicates that diffusion plays an important role in the formation of the colony, most of the Ge growth taking place near the Al rim. Local energy-dispersive x-ray analysis shows that the Al rim contains a fairly high concentration of Ge atoms, of the order of 0.10. This is much higher than the limit of solubility of Ge in Al at the temperature of annealing (less than

0.01), but at the same time much smaller than the concentration of Ge in the surrounding amorphous matrix.

Electron diffraction performed over a large fraction of the colony shows (Fig. 1 inset) continuous rings (Ge) and small arcs (Al). Hence all Al crystallites in the colony have essentially the same orientation, and we must conclude that the colony's growth started from the nucleation of a single Al crystallite. This is reasonable as we know from the granular structure observed at lower concentrations that Al nucleates preferentially to Ge. What is remarkable, however, is that the orientation of the original nucleus is conserved in further growth of the colony, in spite of its complex structure. Since the
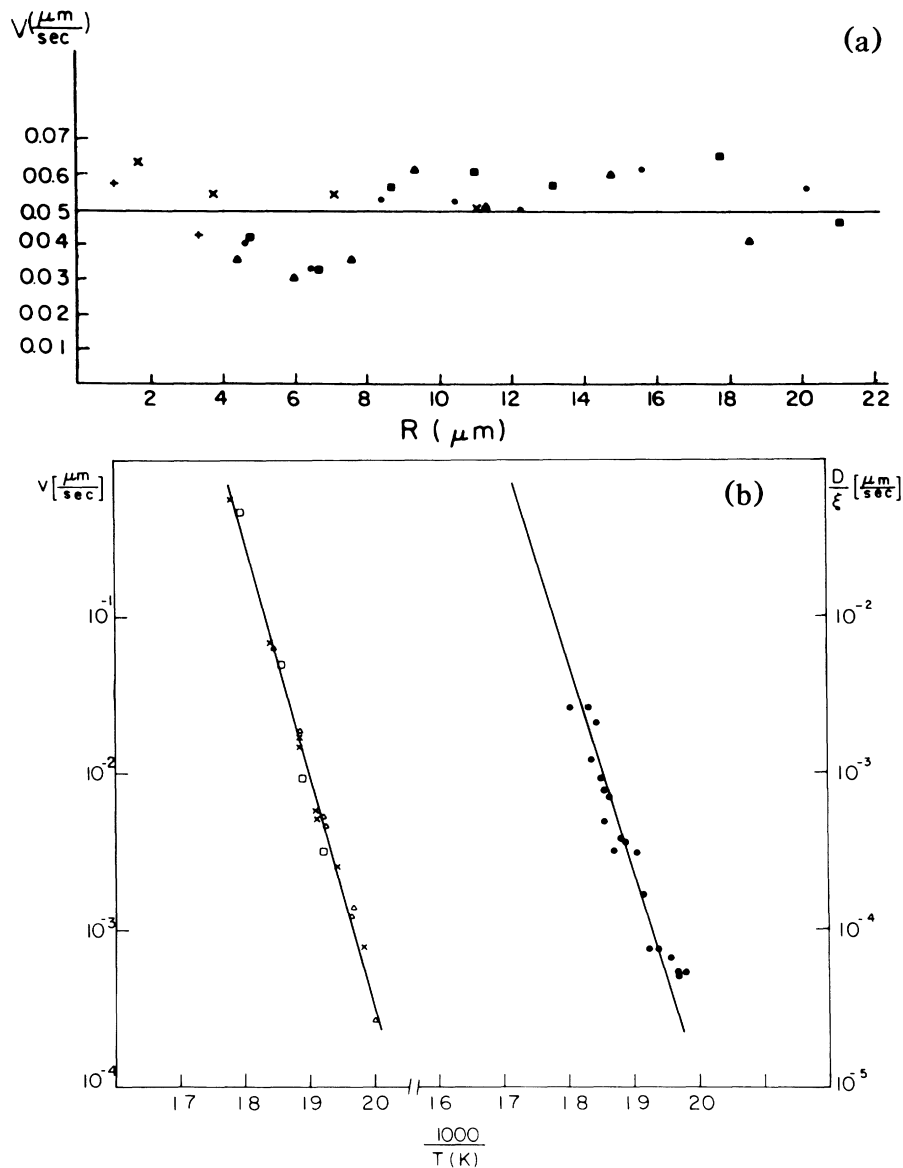

FIG. 2. (a) Growth velocity v as a function of the colony's size at a fixed temperature. The velocity is constant in the steady-state regime. (b) Temperature dependences of the growth velocity and of the ratio of the coefficient of diffusion of Ge in Al, D, to the thickness of the Al rim ξ. ξ has been determined through a measurement of the radial density of the Ge crystalline phase, as the scale over which the density rises from 0.1 to 0.6 of its bulk value.

Al rim contains a high concentration of Ge, it is reasonable to assume that this was also the case for the original nucleus, and that further growth was accompanied by precipitation of the excess Ge in the form of Ge crystallites of random orientation in the interior of the nucleus.

Observation of the colony's growth up to large sizes (or the order of the grid's openings, i.e., 50 μm) implies a low nucleation rate for new colonies. It is then very difficult to catch one of them at the early nucleation stage, such events being few and far apart. However, we have been able to observe that at the fairly early stages of growth, one cannot identify a branched Ge core and an Al rim. Only colonies of sufficient size show this structure, which then represents a form of steady-state growth after the colony has reached "maturity."

The theory paper that follows deals mostly with this steady-state growth mode. Experimentally, it is characterized by a length scale (the average thickness of the rim or the thickness of the fjords) that remains constant during growth at a fixed temperature, which is linear in time [Fig. 2(a)]. This leads to the natural assumption that growth of the Ge core is limited by the diffusion of Ge through the Al single-crystal rim. On very general grounds, one may then expect that the thickness of the rim should be of the order of D/v, where D is the coefficient of diffusion of Ge in Al and v is the growth velocity. This is indeed one of the predictions of the theory,[3] which we have tried to verify experimentally. It turns out that both v and $1/\xi$ increase exponentially with temperature [Fig. 2(b)], with activation energies respective of 3 [Fig. 2(b)] and 1.5 eV (not shown). The temperature dependences of v and D/ξ are compared in Fig. 2(b), where they are seen to be certainly compatible (for the activation of D we have taken the value of 1.5 eV from Peterson and Rothman.[5]) We claim that this gives convincing evidence that diffusion of Ge atoms through the Al rim indeed controls the growth of the colony, one of the basic assumptions of the model presented in the following paper.[3]

While the activated nature of v is not surprising in view of the role played by diffusion in the growth of the colony, its high value is not so easy to understand. Naively, one could have guessed that it should be equal to that of D, and accordingly ξ would have been temperature independent. This expectation is certainly not borne out by the experiment, and indeed the theoretical prediction is different and involves the reaction rate between the Ge in solution and the crystallized Ge. The calculated activation energy for v is the average between that of D and that of the reaction rate. Experimentally, one finds that the activation energy for v is larger than that for D (about twice as large). The theoretical result then implies that the reaction rate is strongly activated. The observed temperature dependence of ξ is, of course, consistent with this conclusion, since we have already shown that it follows the temperature dependence of

D/v.

The understanding of the activated nature of the reaction rate requires a microscopic model for the growth which is not yet available. However, further insight on the microscopic growth mechanism can be gained by our carefully monitoring the growth of the Ge core near its boundary. Figure 3 is a dark-field electron micrograph of Ge crystallites near that boundary. The bright areas are Ge crystallites with a specific orientation selected in the dark-field procedure. The Al rim appears as a pale greyish border. It is clearly seen that the new Ge crystallites appear only at the Al-Ge interface, and not inside the Al rim. The Ge core grows locally either by epitaxial
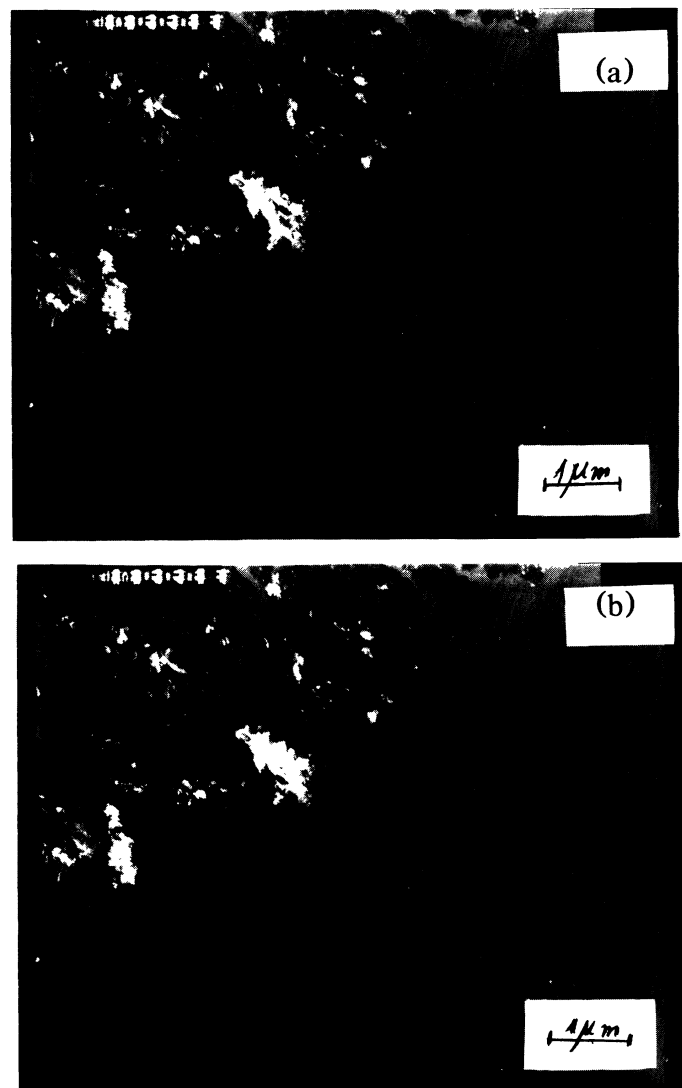

FIG. 3. Dark-field microscopy showing Ge crystallites near the edge of the colony. The two pictures were taken in sequence. Note that the Ge crystallites deep in the interior of the colony have not grown, while new ones have nucleated at the Al-Ge interface.

addition of Ge atoms to a given Ge crystallite in direct contact with the Al rim, or by nucleation of new Ge crystallites at the Al-Ge interface. Both processes clearly take place. The progressive screening of a given Ge crystallite by the nucleation of new Ge crystallites at its boundary limits its own growth. The typical distance between Al fjords appears to be that of the largest Ge crystallites. A detailed microscopic understanding appears necessary for the interpretation of the scale of the structure and of its temperature dependence.

Nucleation of new Ge crystallites at the Ge-Al interface is an essential feature of the described phase separation and growth mode. It of course leads to the polycrystalline structure of the Ge core. We suggest that the activation energy for this nucleation is responsible for the decay of the characteristic length scale at high temperatures, a faster nucleation rate resulting in faster screening and growth stop of a given Ge crystallite, and therefore in a finer scale.

By counting the number of new Ge crystallites formed per unit time at different growth velocities (i.e., at different temperatures), we have determined that the nucleation rate varies faster with temperature than the velocity. The activation energy for the nucleation rate appears to be about 1.3 times larger than that of the growth velocity. This result is in good agreement with the theoretical prediction that $v \propto (DB)^{1/2}$, if one assumes that the activation energy for B is the same as that of the nucleation rate.

The growth of the single-crystal Al rim also presents some very interesting features which will be described in a separate publication. However, this growth does not appear to be a limiting factor for the growth of the colony as we have described here.

In conclusion, we propose that the dense branching morphology is the result of three basic features: (1) atomic diffusion of Ge in Al, (2) competition between diffusion-controlled crystallite growth of Ge and nucleation of new Ge crystallites at the Al-Ge interface, and (3) seeming absence of any important role played by the Al-Ge interfacial energy and its anisotropy in determining the dendritic structure of the Ge growth. Obviously this surface energy has to be reasonably small, as otherwise it would presumably prevent the growth process we observe; and it has to be large enough to prevent observable Ge nucleation in the Al ring. The second feature differentiates this growth mode both from diffusion-limited aggregation (no crystallization, no nucleation), and from dendritic growth (crystallization but no new nucleation).

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[2]E. Ben Yakov, G. Deutscher, P. Garek, N. Goldenfeld, and Y. Lereah, Phys. Rev. Lett. **57**, 1903 (1986).

[3]S. Alexander, R. Bruinsma, R. Hilfer, G. Deutscher, and Y. Lereah, following Letter [Phys. Rev. Lett. **60**, 1514 (1988)].

[4]G. Deutscher, in *Proceedings of the Ninth International Vacuum Congress, Madrid, Spain, 1983*, edited by J. L. de Segovia (Imprenta Moderna, Madrid, 1983), p. 344.

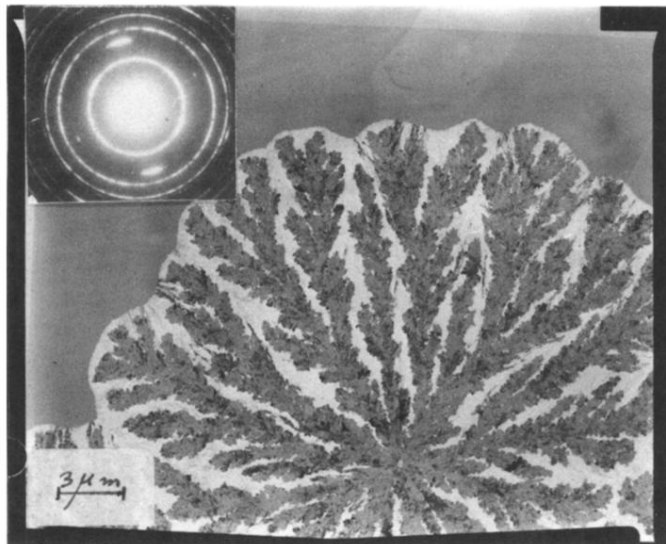[5]N. L. Peterson and S. J. Rothman, Phys. Rev. B **1**, 3264 (1970).

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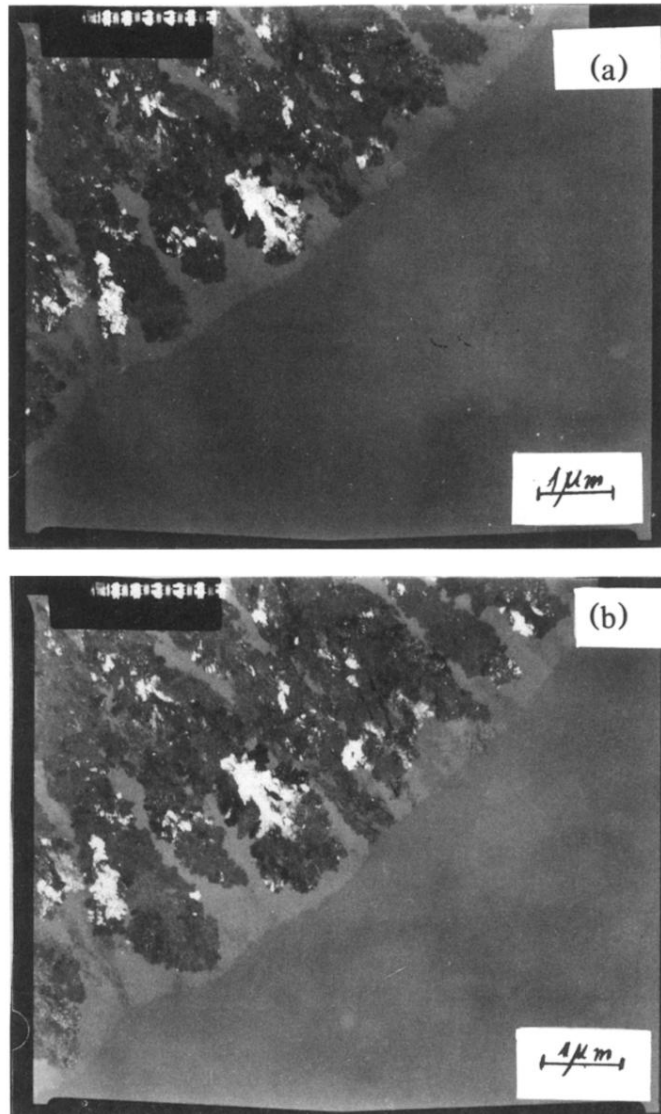
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