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# Pattern Formation on the Free Surface of Bilayer Films

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## 1. Introduction

It is known that the crystallization of amorphous Ge (a-Ge) or amorphous Si (a-Si) in contact with such metals as Ag, Al, Au, etc. takes place more easily than that out of contact: for example, the crystallization temperature (in degrees Kelvin) of a-Ge sometimes decreases to even a half by the contact with Au or Al. Such a type of crystallization is usually called metal-contact induced crystallization or metal-mediated crystallization (MMC in short). While MMC proceeds, a new crystalline phase of Ge or Si (c-Ge or c-Si) appears in the form of aggregates which exhibit impressive patterns [1-3]. The present paper describes the experimental results on the pattern formation of c-Ge or c-Si aggregates which appear on the free surface of bilayer films of Ag-Ge, Al-Ge, Ag-Si and Al-Si in the course of MMC because of annealing.

## 2. Experimental

The bilayer films were obtained with vacuum evaporation or sputter deposition technique. A layer of Ag or Al was formed on a layer of Ge or Si deposited on a $SiO_2$ substrate beforehand. The outer layer of Ag or Al was polycrystalline and 10-100 nm in thickness, while the inner layer of Ge or Si was amorphous and 25-100 nm in thickness. Annealing was performed inside the two-phase region of the equilibrium phase diagram of each binary alloy system in a vacuum of $10^{-6}$ Pa. Since each bilayer film was adhered to $SiO_2$ substrate during annealing, such expressions as Al/Ge/$SiO_2$, etc. will be used hereinafter. Pattern evolution on the free surface was observed with scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

## 3. SEM Observations

Figure 1 illustrates the SEM images of several kinds of patterns of c-Ge or c-Si aggregates observed on the free surfaces of annealed bilayer films in the course of MMC. It can clearly be seen in this figure that the variation of aggregate patterns strongly depends on the alloy system.

On the surface of annealed Al/Ge/$SiO_2$ bilayer film, a number of circular patterns exhibiting complex substructures appear as shown in Fig. 1-a. Each pattern is formed by the aggregation of Ge atoms that doubtless come from the inner a-Ge layer and spread over the free surface of Al layer. In the course of further annealing, the nucleation and growth of aggregates proceed. Each aggregate grows radially, keeping the outward edge circular, and impressive patterns develop radially with repeating ramifications. The radial growth stops just before two aggregates meet. The boundary is stable for a certain period of annealing.

Another example of patterns of c-Ge aggregates is observed in annealed Ag/Ge/$SiO_2$ bilayer film (Fig. 1-c). A number of patterns having many branches appear here and there on the free surface of Ag. In the course of further annealing, both the number and the size increase. The individual pattern bears a resemblance to the pattern formed through diffusion-limited-aggregation (DLA pattern) that is a well-known example of fractal patterns. The fractal dimension $D$ is 1.6, which is about the same to the $D$ value of 1.7 for DLA.

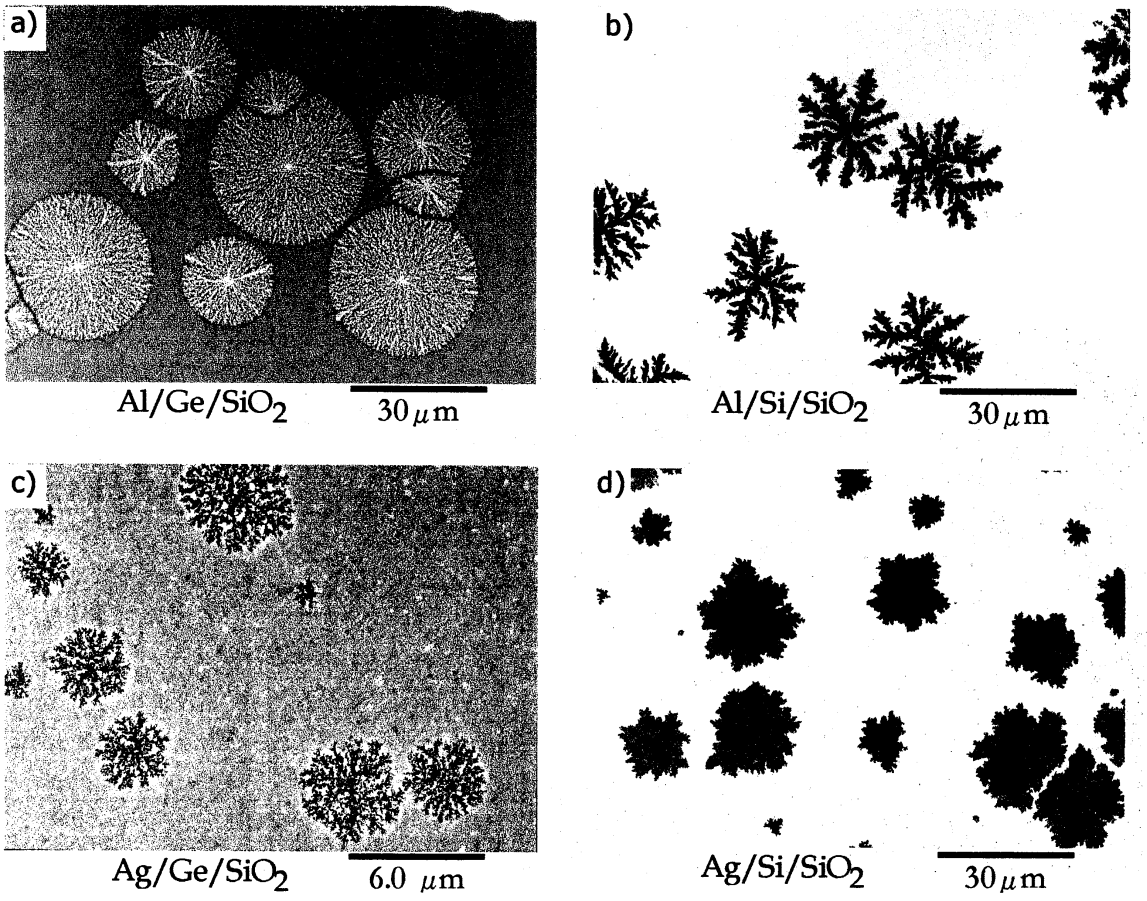


Fig. 1. SEM images illustrating different kinds of patterns of c-Ge or c-Si aggregates which appear on the free surface of bilayer films because of MMC.

When the $Ag/Si/SiO_2$ bilayer film is annealed, a number of black patterns of c-Si aggregates appear on the free surface (Fig. 1-d). Si atoms, of course, diffuse out from the inner a-Si layer. In the course of further annealing, both the number and the size of patterns increase, that is, the nucleation and growth of c-Si aggregates take place in succession. Each aggregate has an uneven periphery but grows radially. When the upper Ag layer is replaced with Al layer, the pattern of c-Si aggregates becomes

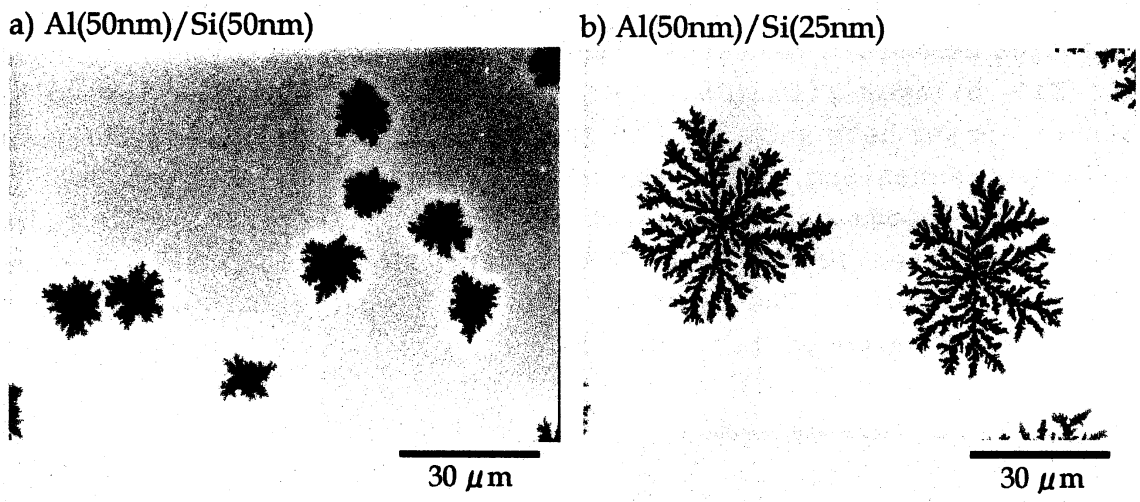


Fig. 2. SEM images illustrating the difference in c-Si aggregate patterns due to the difference in the thickness of a-Si layer of $Al/Si/SiO_2$ bilayer films.

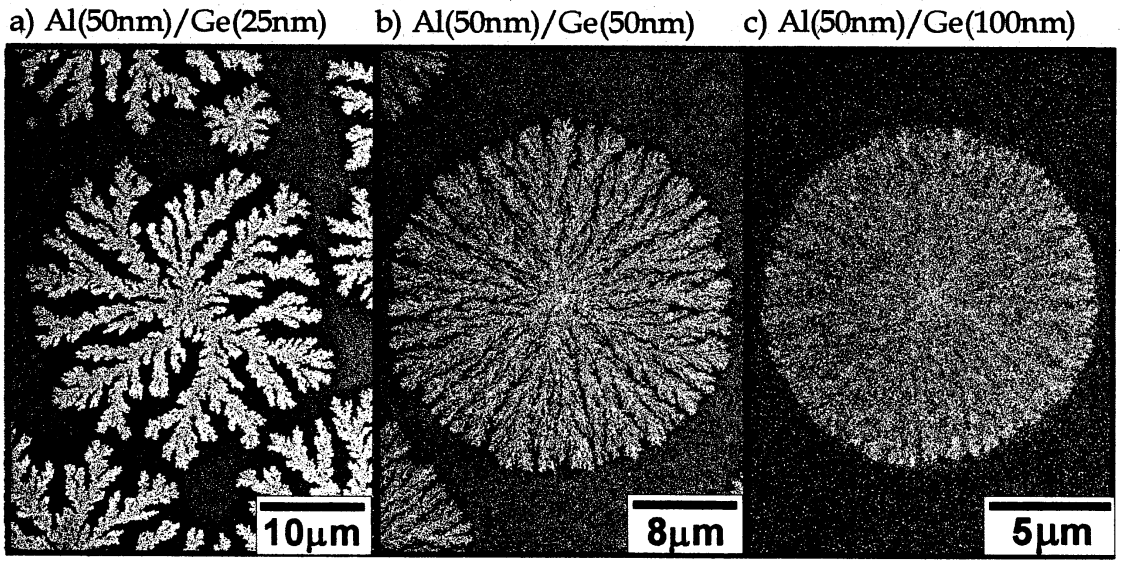


Fig. 3. SEM images illustrating the difference in c-Ge aggregate patterns due to the difference in the thickness of a-Ge layer of $Al/Ge/SiO_2$ bilayer films.

to bear fractal nature as shown in Fig. 1-b, but the branches are thicker and distributed more thinly than those in Fig. 1-c.

It should be noted that the individual patterns in Fig. 1 are not characteristic of their respective alloy systems. Even when the alloy system is the same, the pattern varies depending on the other factors, e.g. the relative thickness of the metallic layer to the semiconductor layer, as can be seen in Fig. 2. The pattern in Fig. 2-b is the same type to that in Fig. 1-b. However, when the Al layer remains 50 nm but the thickness of a-Si layer increases from 25 nm to 50 nm, another type of c-Si pattern appears because of annealing (Fig. 2-a). This type of pattern is similar to that of Ag/Si/$SiO_2$ bilayer film already shown in Fig. 1-d. Figure 2 clearly indicates that the difference in the relative thickness of Si layer causes the difference in the pattern of c-Si aggregates. The thickness effect on the pattern morphology is also observed in Al/Ge/$SiO_2$ bilayer films (Fig. 3).

## 4. Computer Simulations

Cross-section TEM observations indicate the microstructure changes in the course of pattern evolution in, for example, Al/Si/$SiO_2$ bilayer film, as follows. First, the crystallization of a-Si (i.e. MMC) takes place at the interface between Al and a-Si layers. Next, Si atoms in the crystallized region come out through the grain boundaries of Al layer because of capillary effect, and they spread over the free surface. Simultaneously, Al grains go down to form the inner layer which used to be a-Si layer. A point to be considered is the diffusivity of Si atoms in the grain boundaries and on the free surface. Furthermore, when Si atoms penetrate into the Al layer, the surrounding Al-grains are pushed outward, which generates the pressure (compressive stress) which makes the nearby grain boundaries tight. As the growing front of c-Si aggregate moves forward, the pressure becomes larger and hence the c-Si aggregate should overcome the increasing pressure to grow further. Therefore, we should consider the feedback from the pressure (stress) for the pattern evolution.

A reliable simulation is based on the phase-field method that has been successfully applied by Kobayashi to simulate the dendritic solidification [4]. Here, we should replace the temperature field in his original simulation with the stress field. Regarding the concrete procedures for simulation, please refer to our paper to be published in near future. Figure 4 illustrates the pattern evolution of c-Si aggregates during annealing of Al/Si/$SiO_2$ bilayer films. It is obvious that the computer simulation (the lower figures c, d and e) can successfully reproduce the SEM images (the upper figures a and b).

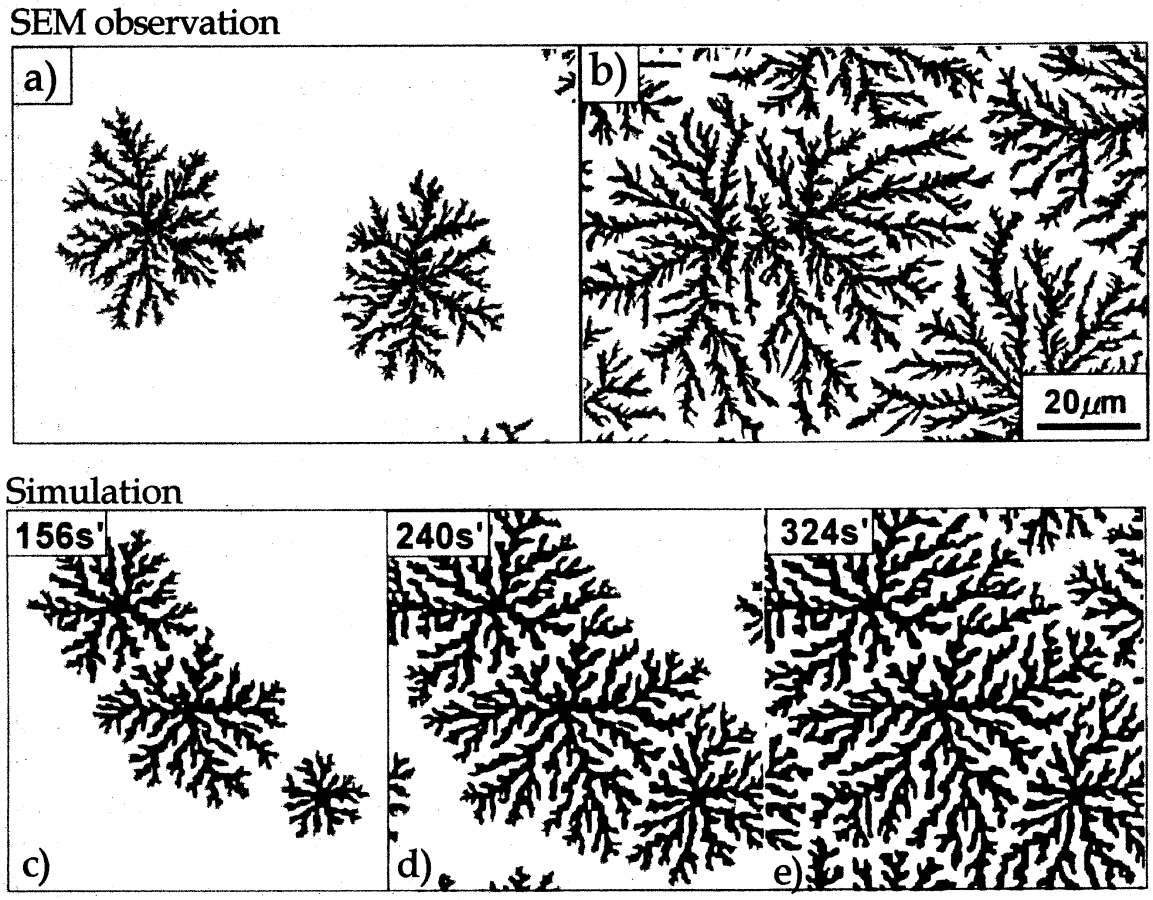


Fig. 4. Pattern evolution of c-Si aggregates in Al(50nm)/Si(25nm)/$SiO_2$ bilayer films: SEM images after annealing at 498 K for 28.8 ks (a) and 460.8 ks (b); simulation results based on the phase-field method (c, d, e).

## 5. Concluding Remarks

It is certain that the impressive pattern of c-Ge or c-Si aggregates which appear because of MMC in (Al or Ag)/(a-Ge or a-Si) bilayer film is a result of the dissipative microstructure governed by the non-linear feedback from the stress around the growing front of the aggregates in the polycrystalline Al or Ag matrix. This paper described only preliminary calculation results. However, the present author's group is now reconsidering the model mechanism of patter formation and then new simulation results will be presented in near future.

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## References

[1] Doi, M., Suzuki, Y., Koyama, T., and Katsuki, F., 1998, "Pattern evolution of crystalline Ge aggregates during annealing of an Al/Ge bilayer film deposited on a $SiO_2$ substrate", *Philos. Mag. Lett.*, **78**, 241.

[2] Doi, M., Kato, K., Yamada, Y., Inaba, H., and Ueda, Y., 1998, "Microstructure changes in bilayer films of phase separation type alloy systems", *Proc. 3rd Pacific Rim Int. Conf. on Advanced Materials and Processing (PRICM-3)*, ed. M. A. Iman et al., (Warrendale, PA: TMS), p. 2069.

[3] Doi, M., 1999, "Pattern evolution of crystalline aggregates of Ge or Si during annealing of Ag/Ge, Al/Ge and Al/Si bilayer films", *Slow Dynamics in Complex Systems*, ed. M. Tokuyama and I. Oppenhaim, (Woodbury, NY: AIP), p. 285.

[4] Kobayashi, R., 1993, "Modeling and numerical simulations of dendritic crystal growth", *Physica D*, **63**, 410.