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Fractal clusters and self-propagating high-temperature synthesis in thin Al/Ge films

V. G. Myagkov and L. E. Bykova
L. V. Kirenskiĭ Institute of Physics, Siberian Branch of the Russian Academy of Sciences, 660036 Krasnoyarsk, Russia

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Fractal clusters in amorphous thin films are examples of growth models. The main models are the Witten–Sander model and its modifications. It is believed that fractal patterns are formed in the course of the crystallization of an amorphous phase. It is shown that self-propagating high-temperature synthesis can be initiated in an Al/Ge film system and fractal patterns are formed in the reaction products. It is conjectured that the transition of an amorphous phase to a crystalline phase does not play a substantial role in the appearance of such patterns, while the formation of fractal clusters is determined by self-propagating high-temperature synthesis. © *1998 American Institute of Physics.* [S0021-3640(98)00605-7]

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Fractal clusters often arise in amorphous films after thermal influences have acted.[1–9] It is believed that the amorphous structure plays an important role in the formation of fractal patterns, where fractal clusters form during a phase transition from an amorphous to a crystalline phase. The most closely studied system in which fractal clusters form is Al–Ge. Two research groups are investigating the formation of fractal patterns in this system. The first group[3,4] is studying the formation of fractal clusters in Ge/Au and Al/Ge bilayer film systems obtained by annealing. The second group[5–9] obtains film samples by simultaneous deposition from two sources. The structure of such films consists of aluminum microcrystallites embedded in an amorphous matrix. After the samples are heated, clusters with a dense branching morphology (DBM) with fractal dimension $d_f = 2$ form. Clusters with a DBM, which occur widely in real systems, have been observed during the crystallization of Al–Ge thin films.[9] For all samples, clusters form in the temperature range 470–500 K. Different growth models have been proposed to explain the nucleation of clusters with fractal morphology in the Al–Ge system. The first group is developing a random nucleation model. The second group is employing in its investigations a combined model consisting of the Eden model and a diffusion-limited aggregation (Witten–Sander) model. Both groups believe that diffusion between aluminum and germanium proceeds in the solid phase.

A large number of materials and compounds has been obtained by self-propagating high-temperature synthesis (SHS) based on powders. The compounds $GeAl_2$ and Ge_5Al_2

have also been synthesized by this method. This reaction is weakly exothermic and therefore requires preheating.[10]

The present letter is devoted to SHS in Al/Ge thin films. It is concluded that SHS, which occurs between layers of aluminum and germanium particles, is the governing process leading to the formation of fractal patterns in bilayer films and in films with a dispersed structure. The specific nature and kinetics of SHS in bilayer thin films are described in Ref. 11, where it is shown that the autowave mechanism of SHS in thin films is similar to the process of explosive crystallization. If a bilayer film system is placed in a uniform temperature field, then above the initiation temperature T_0 a nucleus of reaction products forms on the film surface and propagates along the surface of the sample by a self-maintaining mechanism. Since the formation enthalpy of the reaction products is much higher than the latent heat of the amorphous-to-crystalline phase transition, the temperature at the SHS front is much higher than the temperature of the front in the case of explosive crystallization.

A method of preparing Al/Ge film condensates and a method of initiating SHS in them are described in Ref. 11. Film samples were obtained by successive deposition of a layer of germanium followed by a layer of aluminum on glass or mica substrates 5×10 mm in size and 0.2 mm thick. To crystallize the germanium layer after it is deposited, some samples were annealed for 10 min at 450 °C. This temperature is higher than the crystallization temperature of germanium.[12] Next, a layer of aluminum was deposited on top at a temperature of 50 °C. Al/Ge samples with different layer thicknesses but with a total film thickness of 100–250 nm were used in the experiments.

The samples obtained were placed in a tungsten heater and heated at a rate higher than 1 K/s up to the temperature T_0 at which a reaction started (Fig. 1b). The initiation temperature was in the range 430–500 K. Near the temperature T_0 the velocity V_f of the front was of the order of $(0.2\text{–}0.3)\times 10^{-2}$ m/s and increased strongly with temperature. The temperature T_0 did not depend on the ratio of the layer thicknesses and the total film thickness, but it did depend on the heating rate and the condensate deposition conditions. The SHS process on Al/Ge film samples is similar to the SHS process observed earlier on Al/Ni, Al/Co, and Al/Fe films.[11] After the SHS wave, a second front passed along the reacted sample. The process started at the film edges and propagated toward film center. The velocity of the second front at temperature T_0 was of the order of 0.1 mm/s and increased rapidly with decreasing temperature. In Ref. 11 the temperature of the SHS front was estimated to be higher than the melting temperature of aluminum $T_M(\mathrm{Al}) = 943$ K. For different powder-based systems the SHS temperature does not fall below 1300 K.[10] For this reason, it is surmised that the temperature of the SHS front in the Al/Ge system should also be higher than $T_M(\mathrm{Al})$. Hence it follows that a liquid region, consisting of aluminum and reaction products, exists on the surface of the film. A schematic explanation of this region is given in Fig. 1c.

The surface of the sample is divided conventionally into three parts with different microstructure: the initial part of the sample, the heating zone, and the region of reaction products. Figure 1a shows the microstructure of all three regions. The initial part of the sample has the uniform microstructure of an ordinary aluminum film. Pores 2–8 μm in size appear in the heating zone. Analysis shows that these pores appear in the germanium film and become filled with aluminum (Fig. 1). The microstructure of the reacted samples is diverse and very sensitive to the experimental conditions. For slow heating rates η

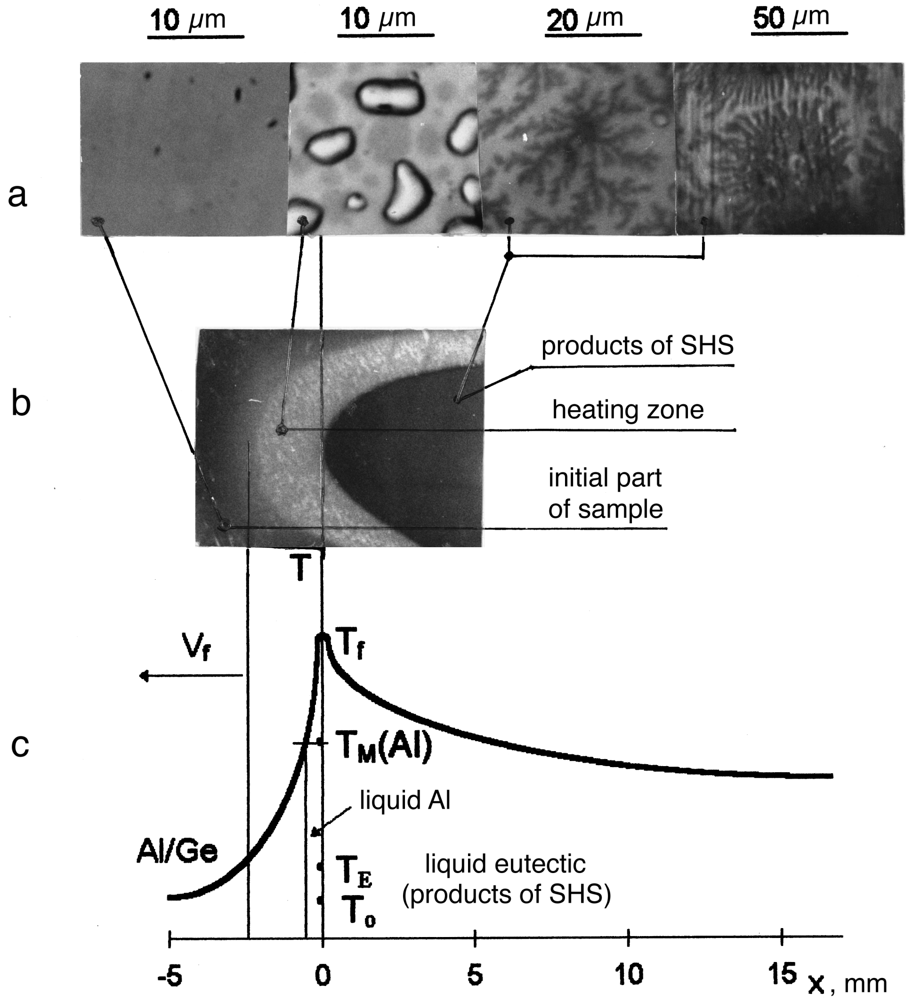

FIG. 1. SHS in an Al(100 nm)/Ge(120 nm) thin-film system. a) Microstructures of the initial sample, the heating zone, and the products of SHS. Only fractal and DBM clusters are shown in the microstructures of the reaction products. b) Photograph of the SHS wave dividing the sample into the initial part, the heating zone, and the reaction products. c) Schematic representation of the temperature front of SHS, elucidating the appearance of a liquid region after passage of the combustion wave.

$\sim$1 K/s up to the initiation temperature and slow cooling the same fractal clusters as those obtained by the first group[4] and the same cluster DBM as that obtained by the second group arise.[6–9] For high rates of heating $\eta \gg 1$ K/s the fractal patterns vanish and a labyrinthine structure appears. The condition of heat removal into the substrate also plays an important role in the formation of the film microstructure. Thus, the samples on whose substrate a germanium layer followed by an aluminum layer were deposited show a uniform microstructure similar to that of the initial film. The experiments show that the crystalline or amorphous state of the germanium film does not influence the kinetics and

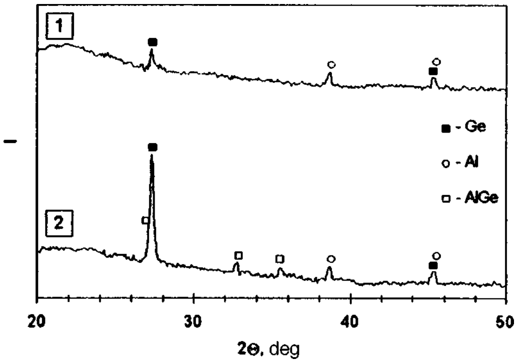

FIG. 2. Diffraction patterns of Al(100 nm)/Ge(120 nm) thin-film samples before (*1*) and after (*2*) passage of a SHS wave.

basic parameters of SHS (initiation temperature, front velocity, microstructure of the reaction products).

This is all based on the following mechanism of SHS in Al/Ge thin films. The temperature of the SHS front is higher than $T_M(\mathrm{Al})$. The temperature of the reaction products is higher than the temperature T_E of the eutectic (Fig. 1c). The formation of pores in the heating zone greatly increases the active contact area between Al and Ge. Intense interlayer diffusion occurs on the SHS front when the temperature of the front is higher than the melting temperature of Al, $T_f > T_M(\mathrm{Al}) = 933$ K. The temperature of the reaction products is also higher than that of the eutectic $T_E = 698$ K. After passage of the SHS wave and after thermal relaxation at a temperature equal to T_E, eutectic crystallization occurs, which gives rise to a second front.[13] This suggests that fractal patterns form from a liquid phase. This does not correspond to the results of Refs. 3–9, where a solid-phase mechanism of fractal cluster formation is studied. The system Al–Ge is a simple eutectic system with a complicated regular microstructure.[13] The initiation temperature of SHS in Al/Ge films in our experiments is equal to the temperature at which fractal clusters appear both in bilayer Ge/Al films[4] and in films obtained by simultaneous deposition.[5–9] This suggests that the fractal clusters studied in these works arise after SHS.

The phase composition before and after the SHS reaction was determined by x-ray crystallographic analysis. Figure 2 shows the diffraction pattern of the initial Al(100 nm)/Ge(120 nm) film with a crystalline layer of germanium and the diffraction pattern of the reacted sample. The diffraction patterns show that the initial Al and Ge layers were polycrystalline. After SHS strong diffraction reflections from germanium and aluminum, corresponding to an increase in grain size, appear and new reflections, which can be interpreted as the appearance of a metastable AlGe phase in the reaction products, arise.[14] The results obtained for films differ from the data obtained for powders,[10] and they confirm the conclusion drawn in the present work that phase separation is observed after eutectic solidification.

On this basis, the initiation of SHS and the formation of fractal patterns in the reaction products should also be expected to occur in other film systems where fractals have been observed.[1,2]

This work pursues two objectives. The first one is to show that SHS can play a determining role in the formation of fractal patterns. The second one is to study the mechanisms leading to the formation of fractal clusters and to improve the understanding of the micromechanisms of SHS.

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