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Multiple self-propagating high-temperature synthesis and solid-phase reactions in thin films

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A variety of self-propagating high-temperature synthesis in thin films has been found and investigated. This modification, called multiple self-propagating high-temperature synthesis, occurs in the solid phase and is a reversible phase transition. Multiple self-propagating high-temperature synthesis is similar in many respects to a metal–insulator phase transition. It is shown that for eutectic systems it is equivalent to a repeated transition through the eutectic temperature of bulk samples. It is inferred that multiple self-propagating high-temperature synthesis in bilayer films is governed by phase separation mechanisms that take place during eutectic solidification and eutectoid decomposition. *© 1999 American Institute of Physics.* [S1063-7761(99)01705-9]

1. INTRODUCTION

Solid-phase reactions in thin films have been an object of investigationin the past,[1] and this activity continues unabated (see, for example, Refs. 2–4). Above all else, they are studied because thin layers are the foundation of modern microelectronics. Solid-phase reactions occur at much lower temperatures in thin films than in bulk samples. The products of solid-phase reactions can be not only compounds but also solid solutions of reagents that result from the mixing of layers.[1,5,6] Layer mixing has also been observed during the formation of quasicrystals[7] and in heterostructures.[8] Searches for optimal heat-treatment temperatures, and times at which these reactions occur, are exclusively empirical.

It is believed that the dominant mechanism of solid-phase reactions is diffusion along grain boundaries. However, such an analysis neglects the possibility that self-propagating high-temperature synthesis (SHS) is initiated in thin films. SHS in powders is well known.[9,10] The kinetics and propagation mechanism of an SHS front in bilayer thin films have been described only recently.[11,12] These papers also show that SHS is a modification of solid-phase reactions in thin films. Previously,[13,14] SHS had been observed in multilayers, where initiation was accomplished by a point heat source. Samples for investigating SHS in bilayer films consist of layers of reagents successively deposited on various substrates. SHS occurs between the layers of reagents if the sample (substrate) temperature T_s becomes equal to the initiation temperature T_0. A nucleus of reaction products forms on the sample, and the SHS front propagates along the sample surface.

Experiments show that SHS comes in two forms in thin films. The first is similar to SHS in powders, where reactions produce compounds with relatively high negative formation enthalpy .[9,10] Thus, for the Al/Ni film system an Ni_2A_3 phase is observed in the reaction products after passage of the SHS wave, leaving no trace of Ni or Al.[11,12] The second is characterized by the emergence of a second front following passage of the SHS wave along the sample. This is followed by phase stratification. SHS in Al/Ge films is of the second type, where the products of the reaction largely contain solid solutions of aluminum and germanium, and only a negligible quantity of metastable phases is formed.[15] After the first SHS cycle, the reagents are therefore mixed. Since the original reagents form after the first cycle, SHS can be reinitiated in the sample. Thus, SHS was initiated about 300 times in a single Al/Ge sample, and could be initiated further. This phenomenon, called multiple SHS, emerges only in type-II samples. The motion of the SHS front and phase separation front can be easy to observe visually. The present paper describes the basic characteristics of multiple SHS and its physical interpretation.

2. EXPERIMENTAL PROCEDURE AND EXPERIMENTAL RESULTS

The procedure for obtaining samples and the method of initiating SHS in bilayer thin films are presented in Refs. 11 and 12. In the experiments, Al/Ge samples obtained by successive deposition of germanium and aluminum films on glass or mica substrates were investigated. The thickness of the germanium and aluminum layers ranged from 40 to 200 nm. The phases formed in the synthesis process were identified with a DRON-4-07 diffractometer (Cu K_α radiation). After a sample is heated to the initiation temperature $T_0 = 550-600$ K in a uniform temperature field, a nucleus of

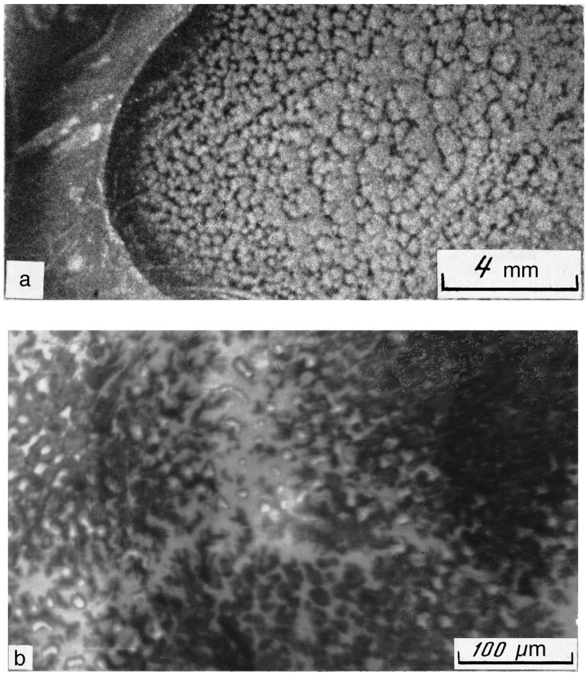

FIG. 1. a) Photograph of an SHS front and DBM clusters in the reaction products of the sample Al(100 nm)/Ge(100 nm). b) Microstructure of a bilayer Al(100 nm)/Ge(100 nm) film sample containing DBM clusters.

a new phase randomly forms on the surface of the sample (Fig. 1a). The SHS front moves along the surface and reflects the temperature topography of the film. The velocity v_f of the SHS front with initiation temperature T_0 is $v_f \simeq 3 \times 10^{-3}$ m/s, and increases with temperature approximately according to the Arrhenius law (Fig. 2). The SHS front can be stopped by reducing the film temperature below the initiation temperature T_0.

A decrease in sample temperature gives rise to a phase separation front, which starts from the boundary left behind by the SHS front. The velocity v_{ph} of the phase separation front increases strongly with decreasing substrate temperature T_s, and starts in the ''soft'' regime (Fig. 2). The emergence of a phase separation front after passage of an SHS wave was first noted in Ref. 15. The first SHS front has a sharp boundary, since there is a difference in reflection from the specular surface of the original film and the surface of the reacted sample, which produces diffuse scattering. The boundary of the subsequent SHS fronts is more diffuse, and it becomes much less appreciable after repeated SHS. Visual observations show that SHS fronts resulting from repeated initiation always start at the same point and mimic the morphological features of the motion of the first SHS front. The phase composition of Al/Ge films does not depend on the number n of SHS cycles (Fig. 3a), but on the thickness ratio of the reagent layers and the velocity of the phase separation front. For $v_{ph} \simeq 1 \times 10^{-3}$ m/s and various n, largely solid solutions of aluminum and germanium are produced; only negligible amounts of metastable phases exist (Fig. 3a). However, for $n=1$ and $v_{ph} \simeq 1 \times 10^{-1}$ m/s, the metastable phases stabilize: an Al_5Ge_3 phase emerges for Al(100 nm)/Ge(100) films (Fig. 3b), and an AlGe phase forms in Al(100 nm)/Ge(120 nm) samples.[15]

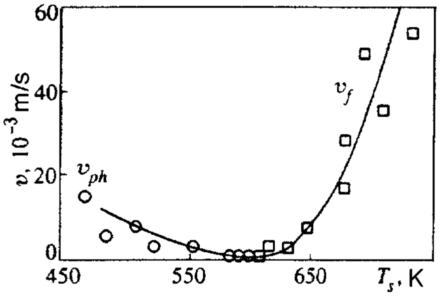

FIG. 2. SHS front velocity $v_f(T_s)$ and the phase separation front velocity $v_{ph}(T_s)$ as a function of substrate temperature T_s.

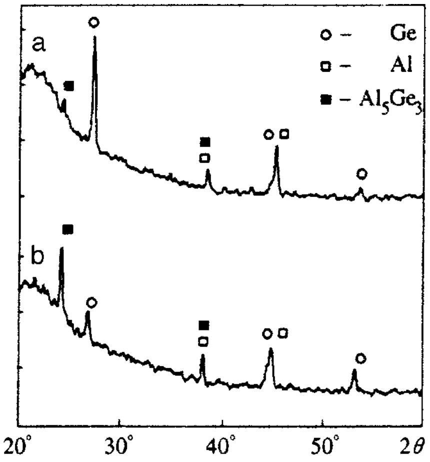

FIG. 3. Diffraction patterns of Al(100 nm)/Ge(120 nm) thin film samples: a) $n=1$, $v_{ph}=1\times 10^{-3}$ m/s; $n=300$, $v_{ph}=1\times 10^{-3}$ m/s; b) $n=1$, $v_{ph}=1 \times 10^{-1}$ m/s.

Investigations show that the temperature T_{ph} at which a phase separation front emerges is the same as the initiation temperature T_0, which is 100–150 K below the eutectic temperature T_E. In bulk sample, the phases separate after eutectic solidification. It is to be expected that the initiation temperature T_0 in Al/Ge films corresponds to the temperature T_E for a bulk Al–Ge alloy. Since the rate of heat removal from thin films is higher than for bulk samples, T_0 should be less than T_E. The initiation temperature T_0 does not depend on the thickness ratio of the reagent layers, just as the eutectic temperature T_E does not depend on the composition of the alloy.

All this suggests that type-II SHS should emerge in bilayer film systems for which the equilibrium phase diagram is of the eutectic type. This was checked for the Pb–Sn system, which has a simple phase diagram of the eutectic type with eutectic temperature $T_E = 456$ K. SHS in a Pb/Sn bilayer film can be repeatedly initiated at $T_0 = 440-450$ K. Stronger evidence can be gleaned from the initiation of multiple SHS in uniform films obtained by deposition of Pb_xSn_{1-x}, Al_xGe_{1-x} alloys $(0.4<x<0.7)$. In this case the initiation temperatures does not depend on x, and are the same as the corresponding temperatures for Pb/Sn and Al/Ge bilayer films. Since the phase separation temperature $T_{ph} = T_0$ in thin films is different from the eutectic temperature T_E, the melting temperature of the film was expected to be the same as either T_0 or T_E.

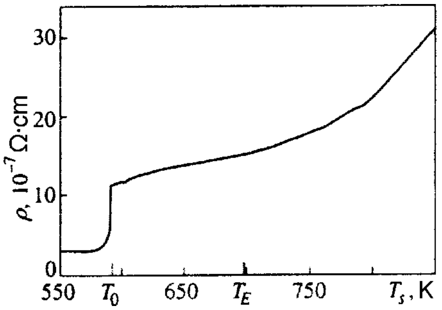

FIG. 4. Resistivity ρ of an Al(100 nm)/Ge(100 nm) bilayer film as a function of substrate temperature T_s.

Figure 4 shows the resistivity $\rho(T_s)$ of an Al(100 nm)/Ge(100 nm) film sample as a function of substrate temperature T_s. It follows from the dependence $\rho(T_s)$ that the Al(100 nm)/Ge(100 nm) sample does not undergo any phase transformations above the temperature T_0. This result was checked directly. The Al(100 nm)/Ge(100 nm) sample was obtained by deposition on a cleavage surface of NaCl, and was then transferred to a glass substrate. Microscopic and visual observations clearly confirm a lack of melting up to $T_s = 850\,\mathrm{K} > T_0$. This is surprising, since phase separation in bulk samples results from eutectic solidification. Nevertheless, multiple SHS in thin films occurs in the solid phase, and is similar to a repeated transition through the eutectic temperature in bulk samples.

The existence of phase separation is also confirmed by resistivity measurements on a film sample as a function of substrate temperature T_s and the number of SHS cycles. Figure 5 shows the resistivity ρ of an Al(100 nm)/Ge(100 nm) film as a function of temperature T_s for three SHS cycles. After initiation of SHS at $T_s > T_0$, the resistivity of the sample increases. At $T_s < T_0$ the resistivity of the sample returns to its original value. The fact that the resistivity of the sample is the same before and after SHS, and that it is the same as the resistivity of the aluminum layer, confirm that aluminum forms a percolation cluster in the film after phase separation. Repeated initiation of SHS increases the initial resistivity somewhat; this might be due to oxidation of the sample by residual oxygen. Multiple SHS is also observed in Al/Si ($T_0 \simeq 700\,\mathrm{K}$), Al/S ($T_0 \simeq 750\,\mathrm{K}$), Al/Zn ($T_0 \simeq 770\,\mathrm{K}$), Au/Ge ($T_0 \simeq 600\,\mathrm{K}$), and Al/Ti ($T_0 \simeq 770\,\mathrm{K}$) film systems.

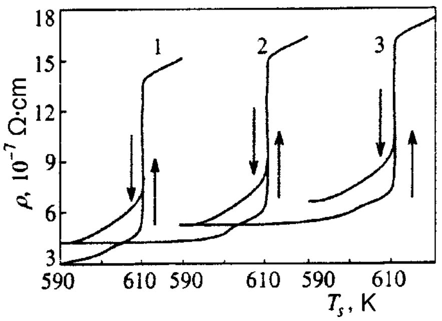

FIG. 5. Resistivity ρ of an Al(100 nm)/Ge(100 nm) film sample as a function of substrate temperature T_s near the initiation temperature T_0 for three SHS cycles. Arrows show the direction of variation of the resistivity.

3. DISCUSSION

The fact that the initiation temperature T_0 is the same as the temperature T_{ph} at which the phase separation front emerges provides a basis for considering the SHS front and the phase separation front to be a single phase-transformation wave. Since during multiple SHS the resistivity changes reversibly and SHS occurs in the solid phase, type-II SHS is a reversible structural phase transition resembling a metal–insulator phase transition. The microstructure of these samples is very diverse, but it consists primarily of clusters with a dense branching morphology (DBM clusters[15]). The microstructure of Al–Ge films was studied in connection with the emergence of fractal formations[16] as well as DBM clusters[17] within them. The intense interest in DBM clusters with fractal dimension $d_f = 2$ is due to the fact that they emerge in many physicochemical and biological systems. In Al–Ge films, DBM clusters comprise a nucleus of polycrystalline germanium, possessing dendritic structure, with single-crystal aluminum disposed among the branches of the dendrite.

The phase separation mechanism in Al–Ge films leading to the formation of DBM clusters was studied in Ref. 17. It is believed that DBM clusters form from an amorphous phase. This agrees with Ref. 18, where it is shown that in Al–Ge films with various concentrations there exists an amorphous phase that transforms into stable aluminum and germanium phases via intermediate metastable phases. The microstructure formed in Al/Ge films depends on the number n of SHS cycles and the velocity v_{ph} of the phase separation front. After the first SHS front has passed and as the phase separation front moves along the surface of the sample, circular nuclei emerge ahead of the front and subsequently merge with the phase separation front. Microscopic investigations show that these nuclei are DBM clusters (see Fig. 1b), which can range in diameter from 10 μm to several millimeters (Fig. 1a). DBM clusters of such sizes are observed during annealing in Bi/Al/Mn/SiO multilayers.[19] At low front velocities ($v_{ph} \simeq 1 \times 10^{-3}$ m/s), laminar microstructure forms perpendicular to the phase separation front. This structure resembles the cellular structure that emerges during directed crystallization.[20]

Investigations of sample surfaces on the substrate side show that SHS proceeds over the entire thickness of the film, even when the layer thickness is $\simeq 1.5\,\mu$m. A total thickness of 3–4 μm is probably the maximum for SHS in bilayer thin films. Subsequent SHS cycles do not alter the original microstructure; this confirms that multiple SHS proceeds in the solid phase.

With long-term initiation of SHS ($n \simeq 300$), the branches of DBM clusters break up and the microstructure of the film becomes uniform. If rapid mass transfer between layers in the first SHS cycle proceeds perpendicular to the film surface, then both SHS and phase separation occur in subsequent cycles along the surface on an interphase boundary between the branches of DBM clusters, which contain germanium, and the single-crystalline aluminum between them. During long-term initiation of SHS, therefore, DBM clusters break down and phase stratification becomes more subtle.

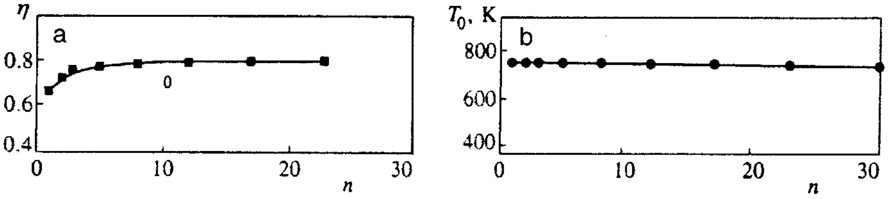

FIG. 6. Degree η of transformation (a) and SHS initiation temperature T_0 (b) of an Al(100 nm) / Fe_2O_3(200 nm) film sample as a function of number n of SHS cycles.

Assuming that diffusion between layers precedes to a depth equal to the thickness of the reagent layer, $d=2\times10^{-6}$ m, and its velocity equals the velocity of the phase separation front $v_{ph}=0.2\times10^{-1}$ m/s, we can estimate the diffusion coefficient during SHS in thin layers to be $D\simeq dv_{ph}=0.4\times10^{-7}$ m^2/s. This is 9–10 orders of magnitude greater than the diffusion coefficient along grain boundaries,[1] and 1–2 orders of magnitude greater than the diffusion coefficient in the liquid phase. The actual value of the diffusion coefficient during SHS can be even higher, so that SHS in thin films must be attributed to explosive chemical reactions.

Explosive chemical reactions in solids resulting from simultaneous uniaxial deformation and shear deformation are described in Refs. 21 and 22. The estimated diffusion coefficient in such reactions is 10^{10}–10^{15} times the value ordinarily observed in the solid phase. The proposed mechanism involves the avalanche-like emergence of structural defects at the instant elastic stresses relax. Such a solid is in a special state that is neither solid, liquid, nor gaseous. At that instant, the solid becomes permeable, and there is enough time for explosive reactions to occur.[21,22] An explosive reaction in the solid phase occurs between Al and Fe_2O_3.[22] The metallic–thermal reaction between Al and Fe_2O_3 has been studied in some depth; its initiation temperature is $T_0=1400-1500$ K, and the front temperature is approximately 2300 K.

In the present work, SHS was studied in Al/Fe_2O_3 bilayer films,which are type-II and have an initiation temperature $T_0=750-770$ K. The bulk abundance of iron in the sample produced after the reaction and the degree η of transformation were determined by the torque method.[6,7] Figure 6a shows the degree η of transformation as a function of the number *n* of SHS cycles. It is clear from the function $\eta(n)$ that the Fe abundance in the sample increases until $n=5$, due to preignition. For $n>5$ the degree of transformation is independent of *n*. This confirms that multiple SHS is not governed by the exothermal nature of the reaction between Al and Fe_2O_3.

The initiation temperature T_0 does not depend on the number *n* of SHS cycles (Fig. 6b). Such dependences $T_0(n)$ are observed in all bilayer film systems in which multiple SHS was obtained. It follows, then, that T_0 in Al/Fe_2O_3 films is analogous to the eutectic temperature of bulk Al–Fe_2O_3 samples. For eutectic solidification and eutectoid decomposition, phase separation often entails the formation of platelike structures, where the plate thicknesses can reach several microns. Multilayers (including bilayer films) are artificial analogs of such platelike microstructures. The kinetics and mechanism of multiple SHS in thin films should therefore be the same as in the case of the formation and decomposition of plate-like structures during transitions near the eutectic temperature or the temperature of eutectoid decomposition of bulk samples.

The following mechanism of multiple SHS in thin films can be inferred from the experimental data presented above. Solid-phase amorphization of the samples occurs after the first SHS front has passed. Below $T_0=T_{ph}$, the amorphous phase decomposes, depending on the velocity of the phase separation front and the thickness ratio. For eutectic systems, there is a correspondence between the phase equilibrium diagram of the reaction products of bulk samples and the characteristics of SHS. The eutectic temperature T_E and the percentage abundance of reaction products determine the initiation temperature T_0 and thickness ratio, respectively, while the liquid eutectic corresponds to the amorphous phase. For $n>2$, SHS does not encompass the entire sample, proceeding instead only at phase boundaries to a thickness of 3–4 μm. Large stresses are produced at the interphase boundary ahead of the SHS and phase separation fronts, producing zones of structural defects. Diffusion is greatly facilitated in these zones, and conditions for explosive reactions set in.[21,22] Metastable phases might play a significant role in the initiation of multiple SHS, since their formation enthalpy can be high.

4. CONCLUSIONS

In conclusion, we note that solid-phase reactions in thin films that are in fact SHS reactions occur only at temperature T_0. Rapid mass transfer and diffusion mixing at the atomic level occur only when SHS and phase separation fronts pass. After the passage of a phase separation front, diffusion in the film sample once again becomes negligible. This suggests that layer mixing, often observed in multilayer (bilayer) films subject to heat treatments and thermal influences,[1,5–8,20] occurs after type-II SHS in these samples. Multiple SHS is a reversible structural phase transition, similar to a metal–insulator phase transition, and can be used in microelectronics devices.

Multiple SHS corresponds to a transition through the eutectic temperature in bulk samples. At present the mechanisms of SHS and solid-phase reactions in thin films are not completely understood. However, the multiple-SHS phenomenon clearly indicates that these mechanisms are related to phase separation mechanisms observed during eutectic solidification and eutectoid decomposition. It is perhaps surprising, considering the many recent studies of solid-phase reactions by various methods, that SHS and multiple SHS in thin films went unnoticed, even though these pheonomena can be observed at atmospheric pressure (no vacuum is required), using straightforward experimental techniques.

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