

# Solid-Phase Reactions, Self-Propagating High-Temperature Synthesis, and Order–Disorder Phase Transition in Thin Films

V. G. Myagkov\*, L. E. Bykova\*, G. N. Bondarenko\*\*,  
V. S. Zhigalov\*, A. I. Pol'skii\*, and F. V. Myagkov\*

\*Kirenskiĭ Institute of Physics, Siberian Division, Russian Academy of Sciences,  
Akademgorodok, Krasnoyarsk, 660036 Russia

\*\*Institute of Chemistry and Chemical Technology, Siberian Division, Russian Academy of Sciences, Krasnoyarsk, Russia

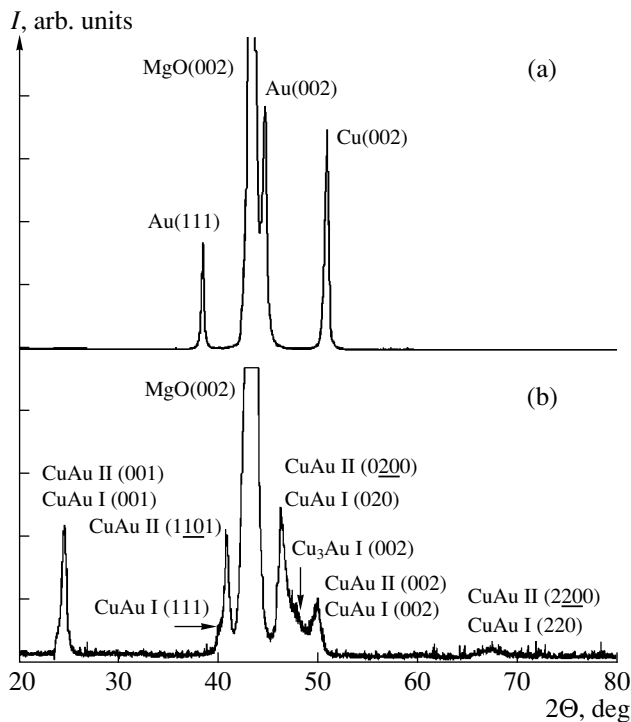
Received January 19, 2000

**Abstract**—The results of experimental studies of self-propagating high-temperature synthesis in double-layer Cu/Au thin-film systems are presented. It is shown that the synthesis initiation temperature for a Cu/Au film is determined by the order–disorder phase-transition temperature in the Cu–Au system. The order–disorder transition temperature for thin films is found to be lower than for the bulky samples. It is assumed that the temperatures of initiation of solid-phase reactions in thin films can be associated with the structural phase-transition temperatures. © 2000 MAIK “Nauka/Interperiodica”.

PACS numbers: 81.30.Hd; 82.65.-i

Solid-phase reactions in thin films proceed at temperatures considerably lower than the relevant temperatures in bulky samples. The majority of solid-phase reactions occur at the interfaces between thin films at temperatures as low as 400–800 K (see, e.g., [1, 2]). However, on long aging, the compounds can form at the contact surface even at room temperature [3]. It is believed that diffusion along the grain boundaries is a dominant mechanism of solid-phase reactions in thin films, because it is several orders more efficient than bulk diffusion. Because of this, diffusion along the grain boundaries and a high defectiveness of thin films may be responsible for considerable mass transport at low temperatures [1]. Since the solid-phase reactions in thin films proceed under nonequilibrium conditions, the phase diagram, as a rule, is not invoked for an analysis of the composition of reaction products and the temperatures of their formation. In practice, it is important to know the formation temperatures, because the thin-film technologies are widely used in microelectronic devices. These devices are often fabricated and operate at temperatures close to the temperature of initiation of solid-phase reactions in thin-film elements. Among the diversity of solid-phase reactions in thin films, there is a class of reactions that occur during the course of fast thermal annealing (see, e.g., [4]). Rapid thermal annealing is part of a rapid isothermal treatment; it amounts to the fast heating of film samples to a certain temperature followed by annealing for 1–100 s at this temperature and subsequent cooling [5]. It is shown in [6, 7] that the solid-phase reactions in thin films can proceed in the self-propagating high-temperature synthesis (SHS) regime. SHS is initiated in double-layer films when the sample temperature  $T_S$

exceeds the initiation temperature  $T_0$  ( $T_S > T_0$ ). SHS is a surface combustion wave propagating along the film surface. At temperatures near the initiation temperature, the SHS-front velocity is equal to  $\sim (2-10) \times 10^{-2}$  m/s. Because of this, the traveling time for the SHS wave in the experimental samples is equal to 5–15 s. This implies that many solid-phase reactions occurring in the course of rapid thermal annealing are the SHS reactions. There are two SHS types in thin films. For the first one, the reaction products contain compounds and only a single SHS wave occurs, as in the case of SHSs in powders. For the second SHS type, the passage of the combustion wave at  $T_S > T_0$  and the lowering of the film temperature to a temperature below the initiation temperature  $T_S < T_0$  is followed by the passage of a second front that is inverse of the SHS front and results in phase layering in the sample. In [8, 9], the SHS of the second type is referred to as multiple SHS (MSHS). MSHS is a reversible structural phase transition corresponding to the transition through the eutectic temperature  $T_E^M$  of bulky samples [9]. However, a film analogue  $T_E^f$  of the  $T_E^M$  temperature is lower than the eutectic temperature  $T_E^M$  of the bulky samples ( $T_E^f < T_E^M$ ). It is conceivable that efficient heat removal to a support reduces the temperature of solid-phase reactions in thin films. Unexpectedly, multiple SHS occurs in the solid phase, where it proceeds with an exceedingly low activation energy [10]. In this case, the compounds are formed at the temperature  $T_0 = T_E^f$  of SHS initiation. It is assumed that the mechanism of phase layering induced by the passage of the front of multiple SHS is related to the mechanisms of phase layering caused by eutectic crystallization and eutectoid or spinodal



**Fig. 1.** X-ray diffraction patterns of a double-layer Au(80 nm)/Cu(55 nm)/MgO(001) film sample; (a) initial sample and (b) after the fast thermal annealing cycle.

decomposition [9]. The result obtained implies that the compounds can form in thin films upon other reversible solid-phase transformations, among which the order-disorder phase transition is most familiar.

This work is devoted to studying SHS in the double-layer films for which the reaction products can undergo the order-disorder phase transition. The study was carried out on a Cu-Au system that is classical as regards the ordering phenomenon. The purpose of this work was to demonstrate that the temperature  $T_0$  of initiation of the solid-phase reactions between the gold and copper layers is determined by the Kurnakov temperature  $T_K$  of a bulky Cu-Au system. The distinctive feature of the Cu-Au system [11, 12] is that, depending on the concentration, the ordered CuAu (superstructure  $L1_0$ ) and  $\text{Cu}_3\text{Au}$  (superstructure  $L1_2$ ) phases form modulated  $\text{CuAu}\parallel$  and  $\text{Cu}_3\text{Au}\parallel$  structures at elevated temperatures in a narrow interval of 25–80 K. For example,  $\text{CuAu}\parallel$  is a one-dimensional modulated structure composed of ten oriented tetragonal  $\text{CuAu}\parallel$  cells arranged along the  $b$ -axis. From the phase diagram [11] it follows that the Kurnakov temperature  $T_K$  changes from 510 to 683 K in the concentration range of 40–60 at. % Au. It is significant that the Cu-Au system exhibits no solid-phase structural transformations other than the ordering phenomenon.

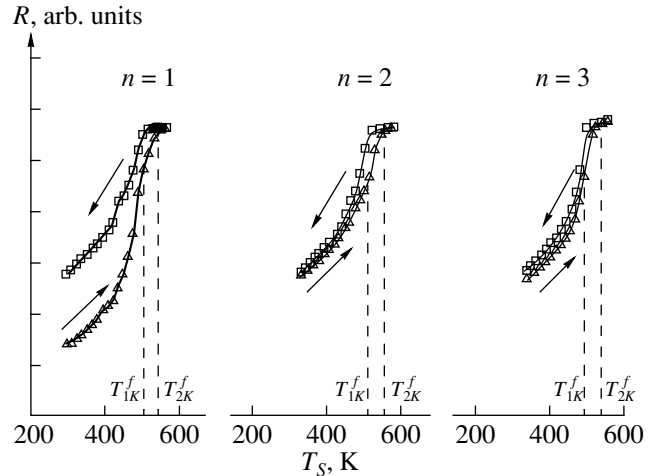
Experimental samples were thin-film systems comprised of copper and gold layers sequentially deposited

on glass mica supports or on a freshly cleaved MgO (001) surface. To produce single-crystal layers on the MgO (001) surface, the first layers were deposited at temperature  $T_S = 500$  K. To avoid reaction between the layers, the second layer was deposited at room temperature. The layer thicknesses were chosen in such a way that the completely reacted samples contained 40–60 at. % Au. The Au/Cu samples thus obtained were placed on a heater and heated at a rate of no less than 20 K/s up to the SHS-initiation temperature  $T_0$ , which turned out to be equal to 520–540 K. The initiation temperature  $T_0 = 520$ –540 K did not depend on the layer thicknesses, which determined the concentration in the reacted sample. In the samples on glass mica supports, the SHS reaction exhibited weakly pronounced auto-wave behavior. The coefficient of reflection from the sample surface changed, allowing visual observation of the course of the reaction. For the samples on the MgO (001) support, the SHS reaction was weakly detectable. Because of this, the samples were subjected to fast thermal annealing consisting of heating to  $T_S = 570$  K  $> T_0$ , exposure to this temperature for 15 s (the time required for the reaction), and slow cooling at a rate of  $\sim 0.05$  K/s.

Figure 1 shows the X-ray diffraction patterns of the Au(80 nm)/Cu(55 nm)/MgO(001) sample corresponding to an approximately 1 : 1 gold-to-copper atomic ratio in the reaction products. The initial samples consisted of epitaxial Cu layers with the (001) orientation parallel to the MgO (001) surface. The upper Au layer grew in two preferable orientations, (001) and (111) (Fig. 1a). The reflections from Au and Cu disappeared after the reaction, suggesting that the layers completely reacted. The X-ray patterns of the reacted Au(80 nm)/Cu(55 nm)/MgO(001) samples show reflections from the ordered tetragonal  $\text{CuAu}\parallel$  phase having the (001), (111), (010), and (110) orientations, as well as the reflections from the orthorhombic  $\text{CuAu}\parallel$  phase with the (100), (1101), (0100), and (1100) orientations parallel to the MgO (001) surface. The  $\text{Cu}_3\text{Au}$  phase with the (100) orientation can form in the reaction products (Fig. 1b). On the whole, the compounds formed in this concentration range corresponded to the equilibrium phase diagram [12]. The relative electrical resistance  $R(T_S)$  of the double-layer Au(80 nm)/Cu(55 nm)/MgO(001) sample is shown in Fig. 2 as a function of the support temperature  $T_S$  for three successive cycles of fast thermal annealing.

The measurements of electrical resistance  $R(T_S)$  (Fig. 2) showed that the smooth change in  $R(T_S)$  was interrupted at  $T_S = T_0 \sim 530$  K because of SHS onset in the film sample at  $n = 1$ . In subsequent cycles ( $n > 1$ ), the smooth  $R(T_S)$  dependence was again interrupted at  $T_S \sim 530$  K. However, it is caused by the order-disorder transition in  $\text{CuAu}\parallel$  and  $\text{CuAu}\parallel$ . In the SHS and the order-disorder-transition regions, the resistance exhibits a slight hysteretic behavior typical of the order-disorder transitions. The slopes of hysteresis branches to

the  $T_S$ -axis in the temperature interval  $(T_{1K}^f, T_{2K}^f)$  likely correspond to the reversible structural  $\text{CuAu} \parallel \longleftrightarrow \text{CuAu} \parallel \longleftrightarrow \gamma$ -solid solution transition, while the temperature  $T_{2K}^f$  corresponds to the  $\text{CuAu} \parallel \longleftrightarrow \gamma$ -solid solution transition. It follows from Fig. 2 that the synthesis temperature  $T_0$  for the thin contacting Cu and Au films coincides with the Kurnakov temperature  $T_{2K}^f$  of the CuAu films ( $T_0 = T_{2K}^f$ ). However, the  $T_{2K}^f$  temperature for the films of equiatomic composition studied in this work turned out to be lower than the Kurnakov temperature of the bulky samples ( $T_{2K}^f < T_K$ ). A plausible explanation is that the temperature curve for the Kurnakov point in thin films is independent of the concentration and goes lower than the pertinent curves for the bulky samples, much as the  $T_E^f$  temperature is lower than the eutectic temperature  $T_E^M$ . An alternative explanation is that synthesis between the gold and copper layers is initiated at the temperature corresponding to the minimum order–disorder-transition temperature in the phase diagram. The  $R(T_S)$  curves shown in Fig. 2 are similar to those for the temperature-dependent resistance of a support at different cycles of initiation of the MSHS fronts [9]. It was shown in [6, 7] that SHS in the thin double-layer films is also initiated upon the deposition of one layer upon the other if the support temperature  $T_S$  in the course of deposition of the second layer is higher than the initiation temperature ( $T_S > T_0$ ). In this case, the synthesis in the Au/Cu film systems is initiated at the same temperature  $T_0 = 520\text{--}540$  K. Note that this method was used for preparing the samples on a fresh NaCl (001) cleavage in the early studies of long-period ordering in CuAu [13]. Nevertheless, the temperature  $T_0$  of synthesis initiation between the Au film and Cu film deposited on top of it was found not to correlate with the ordering temperature. The phase diagrams of the Co–Pt and Au–Cu systems are similar in the equiatomic composition region. In the region of a homogeneous ordered CoPt phase, the Kurnakov temperature changes from 750 to 1070 K, with the maximum value corresponding to the stoichiometric composition. The solid-phase reactions in the Co/Pt/MgO(001) multilayers are initiated at temperatures  $T > 750$  K and result in the ordered CoPt phase [14]. It is shown in [15] that the solid-phase reactions in the double-layer and multilayer Co/Pt films proceed in the SHS regime, with the initiation temperatures  $T_0 = 770\text{--}820$  K coinciding with the temperature of phase ordering in CoPt [16]. This implies that the temperature of initiation of the interlayer synthesis in Co/Pt is determined by the Kurnakov temperature, as in the case of the Au/Cu films. Hence it follows that the initiation temperatures for the film systems exhibiting solid-phase reactions can be associated not only with the order–disorder-transition temperature in the reaction products but also with the temperatures of the other structural phase transformations.



**Fig. 2.** Electrical resistance  $R(T_S)$  of a double-layer Au(80 nm)/Cu(55 nm)/MgO(001) film sample vs. support temperature  $T_S$  for three successive fast thermal annealing cycles. The interruption of the smooth behavior of  $R(T_S)$  in the temperature interval  $(T_{1K}^f, T_{2K}^f) = 520\text{--}540$  K at the first cycle is associated with synthesis onset between the Au and Cu layers. In subsequent cycles, these changes are caused by the order–disorder phase transitions in the AuCu alloy.

In summary, it is shown that the initiation temperature of the Au/Cu film systems is determined by the Kurnakov temperature for the Au–Cu system. This implies that the chemical mechanisms of ordering and synthesis are the same and have a long-range nature. The long-range forces, together with the elastic forces, may be responsible for the formation of the long-period modulated phases that appear upon ordering, spinodal and eutectic decompositions, in the polytypic structures, etc. The results of this study may be of practical importance, because the phase diagram can be used to determine the types of solid-phase reactions and the corresponding initiation temperatures.

#### ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 99-03-32184.

#### REFERENCES

1. *Thin Films: Interdiffusion and Reactions*, Ed. by J. M. Poate, K. Tu, and J. Meier (Wiley, New York, 1978; Mir, Moscow, 1982).
2. L. A. Clevengren, B. Arcort, W. Ziegler, *et al.*, J. Appl. Phys. **83**, 90 (1998); M. Zhang, W. Yu, W. H. Wang, *et al.*, J. Appl. Phys. **80**, 1422 (1996); J. D. Guo, F. M. Pan, M. S. Feng, *et al.*, J. Appl. Phys. **80**, 1623 (1996); H. S. Venugopalan, S. E. Mohny, B. P. Luther, *et al.*, J. Appl. Phys. **82**, 650 (1997); J. S. Huang, K. N. Tu, *et al.*, J. Appl. Phys. **82**, 639 (1997); W. H. Wang, W. K. Wang, *et al.*, J. Appl. Phys. **76**, 1578 (1994); B. I. Boyanov,

- D. T. Goeller, D. E. Sayers, *et al.*, *J. Appl. Phys.* **84**, 4285 (1998); Q. Z. Liu, L. S. Yu, F. Denf, *et al.*, *J. Appl. Phys.* **84**, 881 (1998); J. P. Gambino, B. Cunningham, P. DeHaven, *et al.*, *J. Appl. Phys.* **82**, 6073 (1997); L. Balazs, V. Freury, F. Duclos, *et al.*, *Phys. Rev. E* **54**, 599 (1996).
3. V. Simic and Z. Marincovic, *J. Mater. Sci.* **33**, 561 (1998).
  4. L. J. Chen, I. W. Wu, J. J. Chu, *et al.*, *Appl. Phys.* **63**, 2778 (1988); E. G. Colgan, C. Cabral, Jr., and D. E. Kotecki, *J. Appl. Phys.* **77**, 614 (1995).
  5. R. Singh, *J. Appl. Phys.* **63**, R59 (1988).
  6. V. G. Myagkov and L. E. Bykova, *Dokl. Akad. Nauk* **354**, 777 (1997).
  7. V. G. Myagkov, V. S. Zhigalov, L. E. Bykova, and V. K. Mal'tsev, *Zh. Tekh. Fiz.* **68**, 58 (1998) [*Tech. Phys.* **43**, 1189 (1998)].
  8. V. G. Myagkov, *Dokl. Akad. Nauk* **364**, 330 (1999) [*Dokl. Phys.* **44**, 45 (1999)].
  9. V. G. Myagkov, L. E. Bykova, and G. N. Bondarenko, *Zh. Éksp. Teor. Fiz.* **115**, 1754 (1999) [*JETP* **88**, 963 (1999)].
  10. V. G. Myagkov and L. E. Bykova, *Dokl. Akad. Nauk* (in press).
  11. C. S. Barrett and T. B. Massalskiĭ, *Structure of Metals. Crystallographic Methods, Principles and Data* (Pergamon, New York, 1980; *Metallurgiya*, Moscow, 1984), Chap. 1.
  12. N. M. Matveeva and É. V. Kozlov, *Ordered Phases in Metallic Systems* (Nauka, Moscow, 1989).
  13. H. Sato and R. S. Toth, *Phys. Rev.* **124**, 1833 (1961).
  14. B. M. Lairson, M. R. Visokay, R. Sinclair, and B. M. Clemens, *J. Magn. Magn. Mater.* **126**, 577 (1993); B. M. Lairson and B. M. Clemens, *Appl. Phys. Lett.* **63**, 1438 (1993).
  15. V. G. Myagkov, L. A. Li, L. E. Bykova, *et al.*, *Fiz. Tverd. Tela* (St. Petersburg) (in press).
  16. K. Barmak, R. A. Ristau, K. R. Coffey, *et al.*, *J. Appl. Phys.* **79**, 5330 (1996).

*Translated by V. Sakun*