ISSN 1062-8738, Bulletin of the Russian Academy of Sciences: Physics, 2007, Vol. 71, No. 5, pp. 611–613. © Allerton Press, Inc., 2007.
Original Russian Text © S.M. Zharkov, K.Yu. Malyshonok, 2007, published in Izvestiya Rossiiskoi Akademii Nauk. Seriya Fizicheskaya, 2007, Vol. 71, No. 5, pp. 634–636.

Sequence of Phase Formation during Solid-State Synthesis in Al/Ni Films (Al : Ni = 60 : 40 at %)

S. M. Zharkov[a] and K. Yu. Malyshonok[a, b]

[a] *Kirensky Institute of Physics, Siberian Division, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia*

[b] *Krasnoyarsk State Technical University, Krasnoyarsk, 660074 Russia*

e-mail: zharkov@iph.krasn.ru

Abstract—The structure formed during solid-state synthesis in thin bilayer Al/Ni films with the ratio Al : Ni = 60 : 40 (at %) has been investigated. The films were obtained by thermal evaporation in vacuum with a residual pressure of 10^{-5}–10^{-6} Torr. Solid-state synthesis was performed by diffusion reaction. The sequence of phase formation upon vacuum annealing of bilayer Al/Ni films has been established: Al + Ni $\rightarrow$ Al_3Ni + Ni (T_{ann} = 180°C) $\rightarrow$ Al_3Ni_2 (T_{ann} = 220°C).

DOI: 10.3103/S1062873807050048

Development of microelectronics is related to wide application of thin-film elements. Investigation of reactions in solids between two or several components began a relatively short time ago. Solid-state reactions may significantly affect the microstructure and phase composition of thin films during operation of integrated circuits and other electronic devices. A distinctive specific feature of solid-state reactions in thin films is that they can be initiated at relatively low temperatures (much lower than in bulk samples). Solid-state reaction products can be both compounds and solid solutions of reagents formed as a result of layer mixing. An important question arises in study of solid-state synthesis processes: which of the possible phases is formed first? To date, several different "first-phase rules" have been proposed (see, for example, [1–3]); however, the various experimental data obtained have not yet been explained. Investigation of solid-state reactions is not only of fundamental interest but has also practical importance. For example, Al–Ni alloys exhibit shape memory effect [4], which makes it possible to apply these materials to fabricate microelectromechanical systems, for example, micromotors.

In this paper, we report the results of studying the solid-state synthesis processes occurring in bilayer thin Al/Ni films with the ratio Al : Ni = 60 : 40 (at %). Bilayer films were obtained by thermal evaporation in vacuum with a residual pressure of 10^{-5}–10^{-6} Torr by successive deposition of nickel and aluminum films. The films were deposited on substrates (glass, NaCl) at room temperature ($T = T_r$). The thickness of individual Al and Ni layers were, respectively, 45 and 20 nm. Solid-state synthesis was performed by diffusion reaction: long-term heating for 1 h at a fixed temperature (in the range from 180 to 300°C). Investigation of the film structure and the phase analysis were performed by transmission electron microscopy (TEM) and electron diffraction with a PREM 200 transmission electron microscope.

Electron microscopy study of the bilayer films in the initial state, deposited on a substrate at room temperature (T_s = 17°C), showed that the films obtained consist of crystallites 10–30 nm in size (Fig. 1a). Interpretation of the electron diffraction pattern (Fig. 1b) showed the

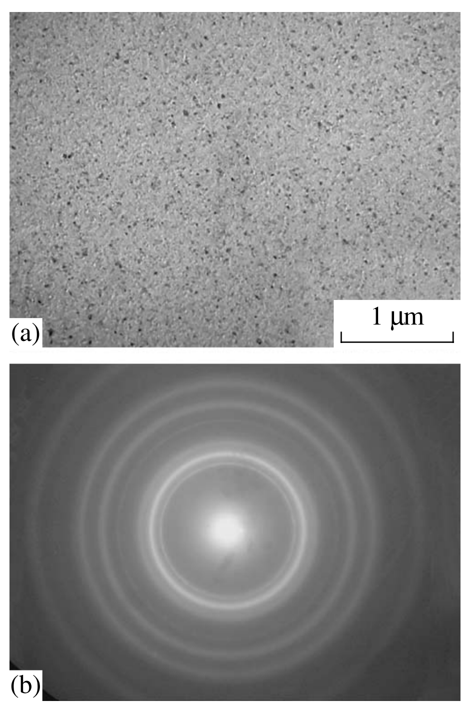

Fig. 1. (a) TEM image and (b) electron diffraction pattern of an Al/Ni film in the initial state.

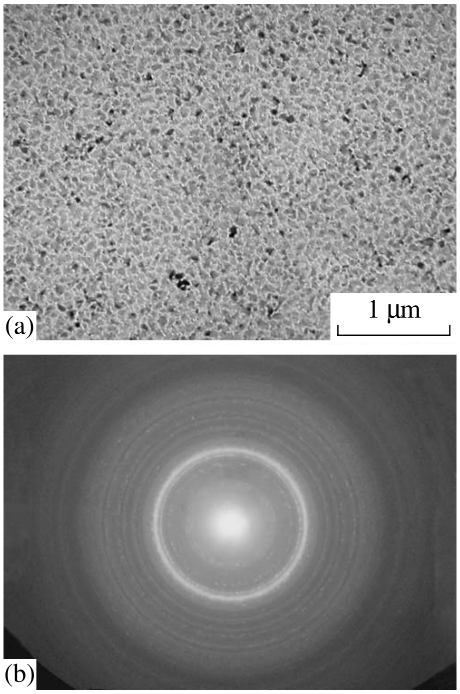

Fig. 2. (a) TEM image and (b) electron diffraction pattern of an Al/Ni film annealed at T_{ann} = 180°C.

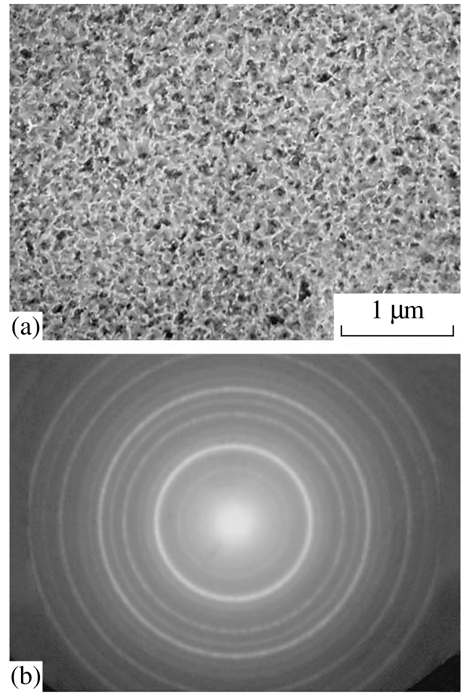

Fig. 3. (a) TEM image and (b) electron diffraction pattern of an Al/Ni film annealed at T_{ann} = 220°C.

presence of the following phases in the films: fcc Ni with the lattice parameter $a = 3.52$ Å (JCPDS card # 04-0850) and fcc Al with the lattice parameter $a = 4.05$ Å (JCPDS card # 04-0787). These phases are characteristic of the bulk state of Ni and Al.

To initiate solid-state synthesis processes, Al/Ni films were annealed in vacuum with a residual pressure of 10^{-5}–10^{-6} Torr at a fixed temperature (in the range T = 180–300°C) for 1 h. Under these conditions, the solid-state synthesis occurred through reaction diffusion.

Interpretation of the electron diffraction pattern of the Al/Ni film annealed in vacuum for 1 h at a fixed temperature (T_{ann} = 180°C) (Fig. 2b) showed that the Al_3Ni phase (sp. gr. *Pnma*) is the first to be formed in the film. This phase has an orthorhombic lattice with the following parameters: $a = 6.60$ Å, $b = 7.35$ Å, and $c =$ 4.80 Å (JCPDS card # 02-0416). Many researchers (see, for example, [5, 6]) believe that the Al_3Ni phase is the first to be formed at the Al/Ni interface during solid-state synthesis. The films annealed at T_{ann} = 180°C contain also the fcc Ni phase (JCPDS card # 04-0850).

The Al/Ni films annealed in vacuum at the fixed temperature T_{ann} = 220°C for 1 h (Fig. 3) contain only the Al_3Ni_2 phase (sp. gr. $P\bar{3}m1$) with the lattice parameters $a = 0.406$ nm and $c = 0.491$ nm (JCPDS card # 14-0648). Further annealing at higher temperatures, up to T_{ann} = 300°C, does not lead to formation of other Al–Ni phases.

Thus, we established the following sequence of phase formations in bilayer thin Al/Ni films with the ratio Al : Ni = 60 : 40 (at %) upon vacuum annealing:

$$\mathrm{Al + Ni \rightarrow Al_3Ni + Ni}\ (\text{at } T_{ann} = 180°\mathrm{C})$$

$$\rightarrow \mathrm{Al_3Ni_2}\ (\text{at } T_{ann} = 220°\mathrm{C}).$$

These results correspond to the ordering rule for Cu_3Au [3], according to which the first phase formed should have the maximum diffusivity. In the case of the Al–Ni system, this is the phase with the highest aluminum content.

It should be noted that the question about the phase that is formed first at the Al/Ni interface during solid-state synthesis processes remains open. Different phases have been reported to be formed first in different studies devoted to the solid-state synthesis in bilayer Al/Ni films: Al_3Ni [5, 6], Al_9Ni_2 [7], Al_3Ni_2 [8], and AlNi [9]. Apparently, this circumstance is related to different conditions of both film preparation and solid-state synthesis initiation.

In [6], on the basis of the rule introduced by Bene [1], it was suggested that the phase with the highest Al content should be formed first during solid-state synthesis in the binary Al/Ni system and the Al content in each subsequent phase formed should be lower than in the previous phase. These conclusions are also consistent with the above-mentioned ordering rule for Cu_3Au [3]. In this case, we can suggest that in Al/Ni films with the ratio Al : Ni = 25 : 75 (at %), along with the Al_3Ni and Al_3Ni_2 phases observed in this study, the following phases will be successively formed at $T_{ann} > 220°C$: AlNi (*B*2 phase), Al_3Ni_5, and $AlNi_3$ (γ' phase).

ACKNOWLEDGMENTS

We are grateful to V.G. Myagkov for discussion of the results. This study was supported by the Russian Foundation for Basic Research, project no. 06-03-32970.

REFERENCES

1. Bene, R.W., *Appl. Phys. Lett.,* 1982, vol. 41, no. 6, p. 529.
2. Theron, C.C., Ndwandwe, O.M., Lombaard, J.C., and Pretorius, R., *Mater. Chem. Phys.*, 1996, vol. 46, nos. 2–3, p. 238.
3. d'Heurle, F.M. and Ghez, R., *Thin Solid Films*, 1992, vol. 215, no. 1, p. 26.
4. George, E.P., Liu, C.T., Horton, J.A., et al., *Mater. Charact.,* 1997, vol. 39, p. 665.
5. Ma, E., Thompson, C.V., and Clevenger, L.A., *J. Appl. Phys.*, 1991, vol. 69, no. 4, p. 2211.
6. Rothhaar, U., Oechsner, H., Scheib, M., and Müller, R., *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2000, vol. 61, no. 2, p. 974.
7. Barmak, K., Michaelsen, C., and Lucadamo, G., *J. Mater. Res.*, 1997, vol. 12, no. 1, p. 133.
8. Bhattacharya, P., Chattopadhyay, K., Bellon, P., and Ishihara, K.N., *Mater. Sci. Eng., A*, 2004, vol. 375–377, p. 1277.
9. Michaelsen, C., Lucadanno, G., and Barmak, K., *J. Appl. Phys.*, 1996, vol. 80, no. 12, p. 6689.