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Highly energetic nonequilibrium microstructure fabricated by ion beam manipulation in the Ag–Pd system

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Abstract

An artificial ordered layered structure of high energy was obtained by a form of ion beam manipulation, namely interface-assisted ion beam mixing, of appropriately designed nano-sized Ag–Pd multilayered films, in which the interfacial free energy elevated the Ag–Pd multilayered films to near to the corresponding highly energetic state. Diffraction analysis suggested that the ordered layered structure consisted of two overlapped face-centred-cubic lattices with lattice constants smaller than those of both pure Ag and pure Pd. The growth mechanism was also discussed in terms of a dynamic atomic collision, followed by a relaxation lasting for an extremely short time, involved in the irradiation process.

In developing new materials showing high performance, great efforts have been made, in recent decades, to fabricate various artificial solid-state microstructures, frequently by means of nonequilibrium and even far-from-equilibrium processes [1]. It is known that in the early 1980s, a scheme named ion beam mixing (IBM) of multilayered films was developed which was capable of producing a variety of nonequilibrium solid phases, mostly with either amorphous or simple crystalline structure [2]. In the multilayered films, there are a certain number of interfaces which possess interfacial free energy. Generally, the interfacial free energy is in positive proportion to the fraction of the interfacial atoms versus the total atoms in the films and is therefore a controllable factor, which can be easily adjusted by changing the number of interfaces while the total thickness of the films is fixed as constant; e.g. by increasing the number of interfaces within a fixed total thickness, the increased interfacial free energy can be used to elevate the initial multilayered films to a highly energetic state. Very recently, a significant development of IBM has been achieved and some new solid-state microstructures have been obtained in some equilibrium immiscible binary metal systems by IBM of multilayered films,

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in which the number of interfaces was increased such that the individual layer thickness was reduced to a couple of nanometres—differing sharply from the typical thicknesses of 5–8 nm in the conventional IBM. Under such circumstances, the atomic migration length required for intermixing and alloying between the constituent metal layers was reduced considerably and was also a couple of nanometres, which helped in forming some new microstructures, e.g. ordered structures obtained in equilibrium immiscible Ag–Co and Ag–Ni systems. A new scheme was thus developed and it was named ion beam manipulation [3].

In this study, the Ag–Pd system was chosen for investigating the possibility of fabricating some new nonequilibrium microstructures by ion beam manipulation. The Ag–Pd system is characterized by a small negative heat of formation ($H_f = -11 \text{ kJ mol}^{-1}$), calculated using Miedema's model at an equiatomic stoichiometry [4] together with a size mismatch of 5%. We present, in this paper, a report on an artificial ordered layered structure obtained by ion beam manipulation in the nano-sized Ag–Pd multilayered films, together with a brief discussion of the formation mechanism of the structure.

On the basis of the calculation of the interfacial free energy [5], three sets of Ag–Pd (with 6, 12 and 18 layers) multilayered samples were designed and prepared by depositing alternately pure Ag and Pd onto NaCl single crystals in an ultrahigh-vacuum (UHV) electron-gun evaporation system with a background vacuum level of the order of 10^{-11} Torr. During deposition, the vacuum level was better than 1.6×10^{-8} Torr. The deposition rate was controlled at 0.5 \AA s^{-1} and during deposition there was no special cooling of the sample holders. The total thickness of all the multilayered samples was about 40 nm: this was designed to match the projected range plus projected range straggling of the 200 keV xenon ions employed in the IBM experiment. The desired overall composition of the Ag–Pd multilayered films, i.e. $\text{Ag}_{50}\text{Pd}_{50}$, was obtained by adjusting the relative thickness of the individual Ag and Pd layers. After deposition, the actual compositions of the multilayered films were confirmed to be $\text{Ag}_{50}\text{Pd}_{50}$ by energy-dispersive spectrum (EDS) analysis within a measuring error around 3%. These results confirmed that the thicknesses of the individual Ag and Pd layers in the deposited films were fairly close to the designed values. It should be noted that the thicknesses of the individual layers of the Ag–Pd multilayered samples were about 4 nm and therefore the atomic migration length for crossing the interfaces for intermixing and alloying in IBM was only a couple of nanometres. The as-deposited films were then subjected to 200 keV xenon-ion irradiation in an implanter with a base vacuum level of the order of 10^{-6} Torr. IBM experiments were conducted with 200 keV xenon ions at room temperature to irradiation doses from 5×10^{14} to $9 \times 10^{15} \text{ Xe}^+ \text{ cm}^{-2}$. The xenon-ion current density was kept around $0.5 \mu\text{A cm}^{-2}$, to avoid an otherwise overheating effect during xenon-ion irradiation. The temperature increase during the IBM was measured to be within 50°C and the effect of the temperature rise on the nonequilibrium structure formation was therefore minor. Transmission electron microscopy examination and selected-area diffraction (SAD) analysis were employed to characterize the microstructural changes emerging in the multilayered films.

For the multilayered films designed to consist of 6 or 12 layers, no new alloy phase was observed after the films were irradiated to doses ranging from $5 \times 10^{14} \text{ Xe}^+ \text{ cm}^{-2}$ to $9 \times 10^{15} \text{ Xe}^+ \text{ cm}^{-2}$. In fact, the structures emerging in the as-deposited state and irradiated films were basically the same for both polycrystalline Ag and Pd, as evidenced by the respective SAD patterns (not shown). In contrast, in the samples with 18 layers, an abnormal structural change was observed after irradiation to a dose of $7 \times 10^{14} \text{ Xe}^+ \text{ cm}^{-2}$. Figures 1(a) and (b) exhibit the SAD patterns for the as-deposited and irradiated states, respectively. From figure 1(a), one can clearly see the sharp diffraction lines reflected from the polycrystalline Ag and Pd of both fcc structures in the as-deposited state and the lattice constants were determined to be $a_{\text{Ag}} = 4.078 \text{ \AA}$ and $a_{\text{Pd}} = 3.875 \text{ \AA}$, respectively, confirming that the initial films were

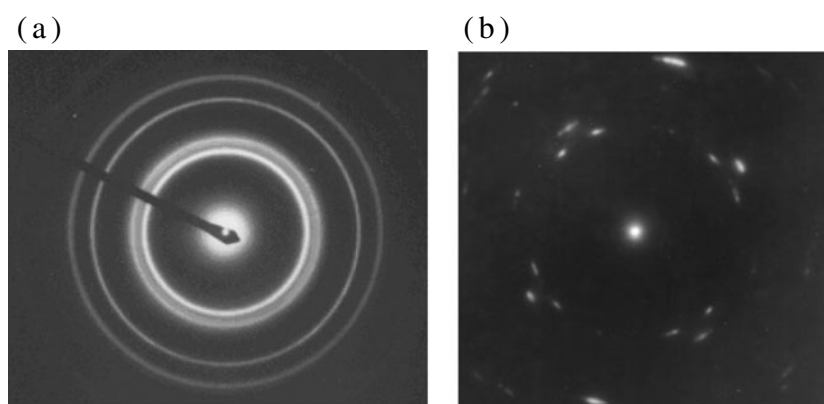


Figure 1. SAD patterns for the Ag–Pd multilayered films consisting of 18 layers: (a) the as-deposited state and (b) after irradiation to a dose of $7 \times 10^{14} \text{ Xe}^+ \text{ cm}^{-2}$.

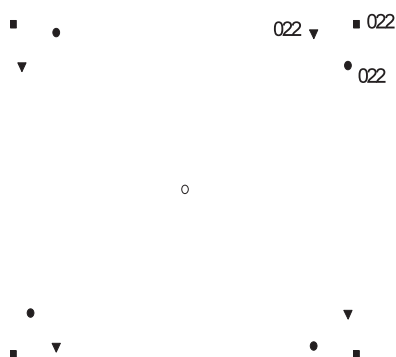


Figure 2. A schematic drawing of the SAD pattern for the Ag–Pd multilayered films consisting of 18 layers after irradiation to a dose of $7 \times 10^{14} \text{ Xe}^+ \text{ cm}^{-2}$.

composed of polycrystalline Ag and Pd. However, in figure 1(b), the SAD pattern contains three sets of diffraction spots, all featuring cubic symmetry. Careful calculation and indexing of the diffraction spots suggested the presence of three overlapping face-centred-cubic (fcc) lattices. Figure 2 is a schematic drawing of the diffraction spots, in which the inner two sets of spots were from two tilted fcc lattices with the same lattice constant, $a_{\text{large}} = 3.403 \text{ \AA}$, while the outside spots were from a small fcc lattice with a lattice constant of $a_{\text{small}} = 2.868 \text{ \AA}$. In other words, three sets of diffraction spots represent two fcc Ag–Pd lattices and the two overlapped fcc lattices can be regarded as an artificial ordered layered structure of high energy, observed, for the first time, in the Ag–Pd system. It is very interesting to note that the lattice constants of the two fcc Ag–Pd lattices were both smaller than those of the pure Ag and Pd lattices ($a_{\text{Ag}} = 4.086 \text{ \AA}$, $a_{\text{Pd}} = 3.890 \text{ \AA}$).

In an effort to understand the underlying physics involved in forming the ordered layered structure, further IBM experiments were conducted. First, to check the effect of the number of layers on the structural change, another two sets of Ag–Pd multilayered films with 12 and 6 layers were subjected to IBM under similar conditions. After ion irradiation up to $9 \times 10^{15} \text{ Xe}^+ \text{ cm}^{-2}$, however, the polycrystalline Ag and Pd remained unchanged and no new microstructure was shown, indicating that the number of layers of the multilayered films

played a decisive role in determining what kind of nonequilibrium microstructure would emerge upon ion irradiation. Since the amount of interfacial free energy was in positive proportion to the number of layers of the multilayered films as mentioned above, it was the interfacial free energy stored in the multilayered films that played a decisive role in forming the ordered layered structure in the Ag–Pd multilayered films. Secondly, the effect of the irradiation dose on structural change was also studied by irradiating the Ag–Pd multilayered films with 18 layers to various doses up to $9 \times 10^{15} \text{ Xe}^+ \text{ cm}^{-2}$. It turned out that the same ordered layered structure appeared at irradiation stages with doses greater than $7 \times 10^{14} \text{ Xe}^+ \text{ cm}^{-2}$. These results suggested that the ordered layered structure was relatively stable upon further irradiation as long as it was formed and therefore the irradiation dose was not a decisive factor in forming the ordered layered structure.

As regards the experimental verification of the role of interfacial free energy in forming some new highly energetic microstructures, there have been a number of papers published reporting the steady-state thermal annealing of multilayered films appropriately designed to show the existence of as well as to demonstrate the significant role of the interfacial free energy [3, 5]. For example, solid-state amorphization (SSA) has been achieved in several systems with positive heat of formation, e.g. Cu–Ta [6], Cu–Nb [7], Cu–W [8] and four Y–refractory metal systems [9–12], where the multilayered films were appropriately designed to include a sufficient fraction of interfacial atoms in the films, in which the individual layer thicknesses were about 2 nm. It should be noted that the claimed observations of SSA in the multilayered films were based on two consecutive structural changes identified by means of diffraction analysis. First, after annealing at a medium temperature (typically 300–400 °C), the sharp diffraction lines (or rings) from the two crystalline metals in the as-deposited films changed into halo(es). Secondly, the haloes changed back to sharp diffraction lines (or rings) upon further annealing at slightly higher temperature (typically 450–500 °C). If only the first structural change was considered, one might attribute the halo(es) to an amorphous oxide. However, if this was correct, the amorphous oxide should have grown via additional oxidation upon further annealing and it would never be possible to transform back to the crystalline metals. In 1999, Kwon *et al* [13] presented direct evidence confirming that SSA did take place in the equilibrium immiscible Cu–Ta system, by transmission electron microscopy examination of a cross-sectional Cu–Ta bilayer sample. These results confirmed that the interfacial free energy did drive the interfacial reaction between the metal–metal layers. In the case of ion beam manipulation, the interfacial free energy stored in the multilayered films did play an important role and therefore was indeed a decisive parameter in the scheme.

In the present case of the Ag–Pd system, the energetic sequence from high to low for the as-deposited Ag–Pd films was deduced to be from the films consisting of 18, 12 and 6 layers, respectively. In fact, following Miedema's model [4] and the method developed by Alonso *et al* [14], the initial free energies were calculated to be 22.5, 14.5 and 6.5 kJ mol⁻¹ for of the Ag–Pd films with 18, 12 and 6 layers, respectively, although the Ag–Pd system has a negative heat of formation. Clearly, the calculation results did confirm that the ordered layered structure corresponded to a highly energetic nonequilibrium state in the Ag–Pd system. In other words, the interfacial free energy was indeed a controllable parameter in ion beam manipulation and it could be used to help in reaching the highly energetic state required for growing the corresponding microstructure. Presumably, for the Ag–Pd multilayered films with 18 layers, the interfacial free energy elevated the initial energetic state of the Ag–Pd multilayered films to a level only a little lower than that of the Ag–Pd ordered layered structure. Ion irradiation not only induced intermixing between Ag and Pd, but also provided additional energy deposited into the Ag–Pd multilayered films and further elevated the films to an energy level higher than that of the ordered layered structure observed in the present study.

We now discuss a possible growth mechanism for the ordered layered structure in the Ag–Pd system. It is commonly recognized that IBM process can generally be divided into two steps, i.e. the first step: atomic collision triggered by impinging ions; followed by a second step: relaxation [2]. In the first step, the irradiating ions triggered a series of atomic collisions, namely an atomic collision cascade, which was responsible for the intermixing between the Ag and Pd metal layers. After an adequate ion dose had been provided, a mixture of Ag–Pd was obtained and it was in a highly energetic and disordered state. According to the atomic collision theory, the relaxation period is extremely short, lasting for only 10^{-10} – 10^{-9} s, which allowed only a limited rearrangement of the atoms in the Ag–Pd mixture, and therefore the mixture could not go straightforwardly to its corresponding equilibrium state; instead, it resided in a possible intermediate state, i.e. the observed ordered layered structure in the Ag–Pd system.

It should be mentioned that some other factors might also influence the formation of the nonequilibrium solid phase or microstructure, e.g. the mechanical stresses due to the size mismatch, interface roughness, the substrate temperature during IBM and radiation-enhanced diffusion. As these possible factors were present for all the multilayered films with different layer numbers in the present study, the above experimental results evidently suggest that the interfacial free energy was a major and controllable factor in manipulation of the ordered layered structure by means of IBM in the Ag–Pd system.

In summary, we have shown that in the Ag–Pd system, interface-assisted IBM can be used to fabricate a new solid-state microstructure, i.e. the ordered layered structure, corresponding to a highly energetic nonequilibrium state; this could be achieved through ensuring an adequate number of interfaces/amount of interfacial free energy for the multilayered films.

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