
**STRUCTURE,
PHASE TRANSFORMATIONS, AND DIFFUSION**

Diffusion in Nanodisperse Layered Film Systems

S. I. Bogatyrenko, N. T. Gladkikh, A. P. Kryshchal', A. L. Samsonik, and V. N. Sukhov

Karazin Kharkov National University, pl. Svobody 4, Kharkov, 61077 Ukraine

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Abstract—The results of studies on diffusion in a layered Cu–Au film system of a variable thickness (20–3 nm) obtained by the methods of electron diffraction, X-ray diffraction, and resistance measurements are given. It has been found that, regardless of the order in which the components are condensed on a substrate, a variable-composition alloy is formed in the contact area even when the substrate is at room temperature. The estimates made on the basis of the data obtained demonstrate that at the characteristic size of the structural elements of the components equal to 2 nm, the effective coefficient of the copper diffusion into gold is $\sim 10^{-15}$ cm²/s, which is much larger than the values known for macroscopic samples. This indicates that the decisive role in the preparation of these systems is played, along with the condensation-induced diffusion processes, by the smallness of the characteristic size, leading to a considerable decrease in the energy of vacancy formation and the corresponding growth of the diffusion coefficient.

Key words: size effect, diffusion, thin films, gold, copper

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INTRODUCTION

Diffusion processes in condensed films (both island and continuous and, especially, in layered film systems) attract particular attention of investigators. This attention is primarily due to the fact that the reproducibility of the properties of these objects and materials on their basis, as well as the reliability of devices and instruments in which such materials are used, are mainly determined by the diffusion processes that take place both during their preparation by condensation and after the condensation has been finished. It has long been known that diffusion processes, which take place during the formation of condensed films, are much more intense than those in layers that have already been formed.

It will suffice to mention that, e.g., in thick condensed copper films that were prepared using high deposition rates at substrate temperatures close to room temperature, the recrystallization begins near the boundary with the substrate already during the film formation [1], whereas in usual macroscopic samples the recrystallization occurred at temperatures above $\sim 0.35T_m$ (T_m is the melting point).

However, if a sufficiently thick condensed film of copper with a nanodispersed structure is brought into contact with a macroscopic sample of metallurgical nickel and this system is annealed, one can observe the effect of a vacancy-flux reversal [2], which consists in that it is nickel that mainly diffuses into the condensed copper film, whereas in macroscopic samples, generally, it is the diffusion of copper to nickel that dominates; i.e., there is observed a change in the relationship between the partial diffusion coefficients and a change

in the sign of the Kirkendall effect due to an extremely fine nonequilibrium structure of the copper films.

Kosevich et al. [3], who studied the mutual diffusion in a layered thin-film polycrystalline Au–Ag system by measurements of electrical resistivity, revealed the effect of the condensation-stimulated diffusion, i.e., the diffusion stimulated during deposition of gold on a silver film due to a substantial increase in the concentration of vacancies, which were generated on the surface of the gold film growing under nonequilibrium conditions. To determine the mechanism of this phenomenon, a detailed study of the condensation-stimulated diffusion was undertaken in [4]. It was found in particular that, depending on the order of the alternation of the layers, the phenomena occurring in the films during condensation can be responsible not only for the accelerated condensation-stimulated diffusion in two-layer films, but also for the condensation-decelerated diffusion. The following explanation was provided for this fact. In a usual two-layer system in the absence of condensation the fluxes of the components *A* and *B* are unequal, since their partial diffusion coefficients are unequal. The difference between the diffusion fluxes of the components is compensated by a vacancy flux toward the faster diffusing component, giving rise to the Kirkendall effect. The presence of a vacancy flux in the diffusion zone causes an increase in the partial diffusion coefficient of the faster component and a decrease in the diffusion coefficient of the second component [4]. If the surface of the growing film during condensation is assumed to be a source of excess vacancies, then there appears a vacancy flux toward the film exposed to condensation. This

vacancy flux changes the ratio between the partial diffusion coefficients of the components. For example, if the component *B* is condensed on a film of the component *A* with a larger partial diffusion coefficient, then the vacancy flux responsible for the Kirkendall effect and the condensation-induced flux will be added, leading to a higher rate of mixing of the *A* and *B* components. If the component *A* is condensed on a film of the component *B*, the vacancy fluxes are directed oppositely, and it is the relationship between them that will determine the value and the direction of the total flux, as well as the corresponding changes in the partial diffusion coefficients. This can probably cause, e.g., a decrease in the mixing rate.

A huge body of studies pertaining to diffusion processes in condensed films [5, 11] and nanocrystalline materials [6] produced of nanoparticles have been performed to date. A considerable increase in the intensity of the diffusion transfer observed in condensed films is usually related to the contribution from the grain-boundary diffusion, since these films generally have an extremely dispersed structure, which has been called a nanostructure, with an enormous contribution from grain boundaries. Studies on the diffusion mobility in compact nanodispersed materials, which are produced by pressing nanopowders, encounter considerable difficulties related to the separation of the contributions from the volume, grain-boundary, and surface diffusion because of the small characteristic sizes of the structural elements.

At the same time, direct investigations of the diffusion mobility in separate nanoparticles are limited because of serious experimental problems. An increase in the diffusion coefficient in such particles, which is caused by a reduction in the energy of formation and, hence, an increase in the concentration of vacancies in fine particles as compared to macroscopic samples, was first noted in [7] when analyzing the size-related reduction of the melting temperature.

These concepts were developed further by other investigators [8, 9, 16], who analyzed the decrease in the lattice parameter in nanoparticles in island films and showed that the decisive role in these objects is played by surface and near-surface vacancies, which mainly determine the diffusion activity of these objects. These data agree with the effect of the volume-to-surface defect transformation in nanoparticles of alkali halide crystals, which was revealed by the method of electron paramagnetic resonance [10].

The high diffusion mobility in nanoparticles was convincingly illustrated by the formation of a homogeneous alloy upon the condensation of gold on copper particles less than 5 nm in size as observed in experiments with island films using the electron diffraction and electron microscopy methods [12]. If the size of the copper particles are larger, a two-phase island film is formed after gold condensation. Obviously, these experiments simultaneously manifest both the effect of the condensation-stimulated diffusion, since the

partial diffusion coefficient of copper is larger than the corresponding coefficient of gold condensing on copper particles [13], and the smallness of the particle size, since a homogeneous alloy is formed only when the size of copper particles is less than a certain value.

Since the understanding of the diffusion processes is very important for ensuring stability and reproducibility of properties of nanomaterials, it seems reasonable to go on with studies on diffusion in nanodispersed layered film systems.

EXPERIMENTAL

In accordance with the task posed, as the objects of the study we chose nanodispersed layered copper–gold film systems produced by a consecutive condensation of the components, which were evaporated from independent sources. This system was chosen because copper and gold are unlimitedly soluble in the liquid and solid states (phase diagram of the “cigar” type) [14]. Their lattice parameters differ substantially ($a_{\text{Cu}} = 0.361$ nm and $a_{\text{Au}} = 0.408$ nm [15]), making it possible to determine the formation of the alloy and find its concentration by diffraction methods with a sufficient reliability. Furthermore, the heat of sublimation of copper (338.7 kJ/mol) is more than two times lower than that of gold (787.1 kJ/mol) [15] and, hence, the partial diffusion coefficient of copper is larger than that of gold (the activation energy for diffusion of copper in gold is 1.19 eV; and for gold in copper, 1.96 eV [12]). Therefore, in line with [3, 4], these factors can be expected to influence the alloy formation when copper and gold layers are deposited in different sequences during consecutive condensation.

The layered film systems were prepared by thermal evaporation of 99.995% pure copper and gold from tungsten evaporators and their subsequent condensation on carbon films—substrates, which were pre-condensed on cleaved facets of NaCl single crystals at room temperature or at 70°C. Samples of different types of the layered systems were studied. For the examination by electron microscopy and electron diffraction, films of different thickness, but with approximately the same component-to-component thickness ratio, were produced. The geometry of the evaporators and the system of movable shields between them and an extended substrate ensured the copper to gold mass thickness ratio from 10 nm : 10 nm to approximately 1 nm : 1 nm in a single experiment.

To measure the electrical resistance of the multilayered Cu–Au film system, copper and gold films having the same mass thickness were deposited alternately on glass substrates with a preliminarily applied copper leads. These substrates were placed in a special holder–heater, which allowed measuring the electrical resistivity of the film system directly during its heating and cooling.

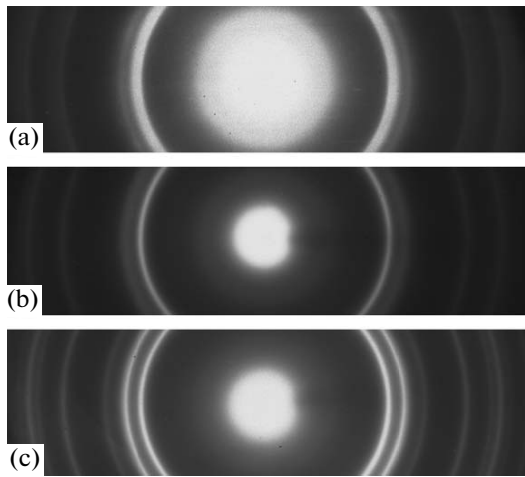


Fig. 1. Electron diffraction patterns of a system consisting of copper and gold films having the mass thickness (a, b) 2 nm and (c) 10 nm. The system was produced by consecutive condensation of (a) copper on gold and (b, c) gold on copper at the temperature of the substrate equal to 70°C.

RESULTS AND DISCUSSION

First, we studied the Cu/Au and Au/Cu systems produced by consecutive condensation of the components on an extended substrate so that the mass thickness of each film changed from 10 nm to 2 nm and their thickness ratio was 1 : 1; i.e., the film systems with the total mass thicknesses from 20 to 4 nm were examined.

When each film of copper and gold was more than ~5 nm thick, an electron diffraction analysis of the layered system clearly revealed two sets of lines, namely, copper and gold lines, regardless of their condensation sequence. If the films were thinner, the character of the diffraction pattern changed differently with thickness, depending on the sequence in which the components were condensed (Fig. 1). The maximum intensities of the lines corresponding to pure gold and pure copper decreased in the film system produced by condensation of gold on a copper film when the films were less than 5 nm thick each. In this case, the position of the maximum in the (111) Au line and the character of its profile on the small-angle side changed only a little, while the intensity of the maximum in the (111) Cu line diminished to such an extent that it actually turned into an inflection point in the photometric curve of the corresponding electron diffraction pattern (Fig. 2). The minimum of the intensity between the maxima in the (111) Au and (111) Cu lines vanished, and the intensity of the (111) Cu line became equal to that of the (200) Au line. An analogous picture was observed for the other pairs of gold and copper lines in the electron diffraction patterns. For example, at a minimum thickness of 2 nm in this series, the minimum between the (200) Au and (111) Cu lines vanished, and the whole space between them

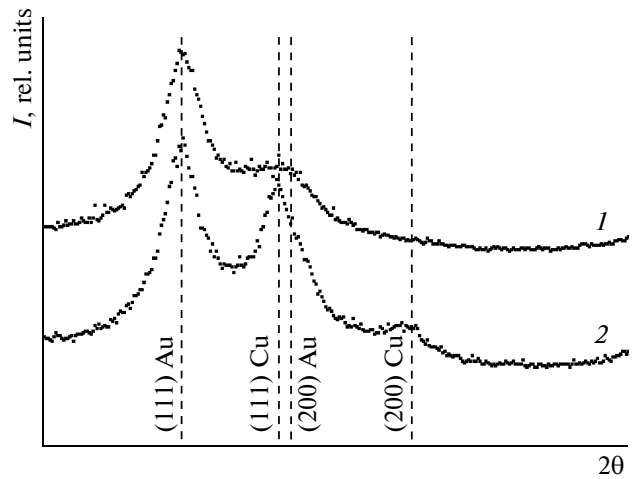


Fig. 2. Photometric curves of the electron diffraction patterns of films produced by consecutive condensation of a gold film (1) 2 nm and (2) 10 nm thick on a copper film (1) 2 nm and (2) 10 nm thick.

turned into a single broad line, whose intensity on the small-angle side coincided with the intensity of the (111) Cu line at this thickness. This is clearly seen from the photometric curves of the corresponding electron diffraction patterns in Fig. 2.

The changes in the diffraction pattern of the layered system produced by condensation of copper on a gold film differed considerably in character as the thickness of the layers decreased. In the first place, the changes began at a smaller thickness. They became perceptible when the copper and gold films were less than 3 nm thick and their character was slightly different.

As before, the position of the maximum in the (111) Au line and its profile on the small-angle side changed insignificantly. The maximum in the (111) Cu line displaced toward the (111) Au line and was approximately midway between the (111) Au and (111) Cu lines at a minimum thickness of the copper and gold films (2 nm each). As can be seen from the photometric curves in Fig. 3, the (111) Au line and the Cu-based (111) line actually form a single broad line with two irresolvable maxima. Similarly to the previous case, the position of the (200) Au line did not change, the maximum in the (200) Cu line almost vanished, and the (200) Au line on the large-angle side smoothly transformed to a background line in the vicinity of the (200) Cu line.

This difference in the diffraction patterns also persisted, depending on the condensation sequence, in the thinner layered systems. For example, when the layers were 1.5 nm thick and Au was condensed on Cu, only the diffraction pattern of an almost homogeneous solid solution was actually observed in the electron diffraction patterns. When copper was condensed on gold, even if the thickness was the same, the diffraction

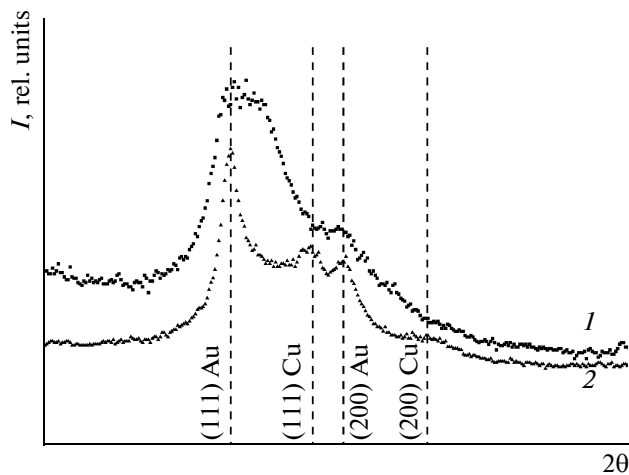


Fig. 3. Photometric curves of the electron diffraction patterns of films produced by consecutive condensation of a copper film (1) 2 nm and (2) 10 nm thick on a gold film (1) 2 nm and (2) 10 nm thick.

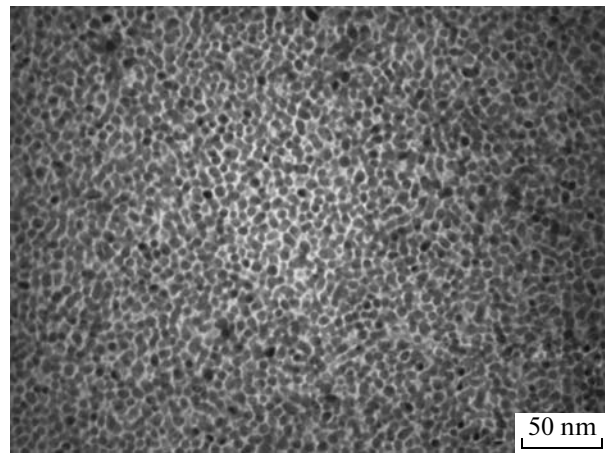


Fig. 4. Electron micrograph of a copper–gold film system (with the mass thicknesses of the gold and copper films being 10 nm each).

line, which emerged due to the mutual approach of the (111) lines of the gold- and copper-based solutions, was much broader; it actually corresponded to two close lines.

Thus, the electron diffraction analysis of the Au–Cu film system demonstrated that no homogeneous alloy was formed even when the mass thickness of the contacting components was small, regardless of the condensation sequence. In both cases, a solid solution whose composition changed across the film was formed; however, the character of the diffusion mixing depended on the sequence in which the components were condensed. When gold was condensed on a copper film, a continuous series of solid solutions was formed across the thickness. When copper was condensed on a gold film, diffusion mixing was also observed, although to a lesser extent, since the copper-to-gold diffusion coefficient decreased because of the different directions of the vacancy flux related to the Kirkendall effect and of the flux running from the condensation front to the substrate [4]. This is unambiguously indicates the important role played by the size effect, namely, the small thickness, in the acceleration of diffusion processes. It turns out that the smallness of the characteristic size (i.e., the size effect) “overrides” the deceleration of the diffusion mobility caused by the condensation process.

The data obtained make it possible to estimate the diffusion coefficient of the more active component, which is copper in this case. If we assume, in accordance with the experimental data, that in the time required for the preparation of the film (usually ~ 10 s) there occurs a diffusion mixing in a layer ~ 1 nm thick, then the expression $x^2 = D\tau$ for the effective diffusion coefficient gives $D \sim 10^{-15}$ cm²/s, which is in agreement with the available literature data [16].

An electron microscopic analysis of the film systems under study showed that the Au–Cu films had an island structure with a characteristic size of islands being much larger than their height (Fig. 4). This structure is natural, since under the conditions used in this study the condensation is implemented through the Volmer–Weber mechanism. However, in these films it is rather difficult to distinguish between the diffusion processes on the free surface, at the interphase boundary, and at the boundary with the substrate; therefore, the values calculated should be viewed as an effective diffusion coefficient in the system under study.

Taking into account that a homogeneous solution was not formed even at a small thickness of the layers when copper was condensed on gold, we performed experiments on measurements of the electrical resistivity of a multilayered Au–Cu film system produced by consecutive condensation of 40 alternating Au and Cu layers with a mass thickness of 2 nm each. In this case, the characteristic size for the most part of the volume of such a film system is 2 nm. Figure 5 presents one of the obtained variations of the electrical resistivity for this layered system subjected to heating–cooling cycles. It is seen that the formation of a homogeneous solid solution was almost complete already after the first heating–cooling cycle. This is confirmed by a reproducible behavior of the resistivity in the subsequent cycles.

This conclusion is also supported by X-ray diffraction analysis of this layered film system after heating and cooling (Fig. 6); according to this analysis, the lattice parameter of the Cu–Au alloy corresponds to 44 at % Au, which is in agreement with the initial ratio between the thicknesses of the copper and gold films.

An analysis of the variation of the electrical resistivity in a heating–cooling cycle makes it possible to

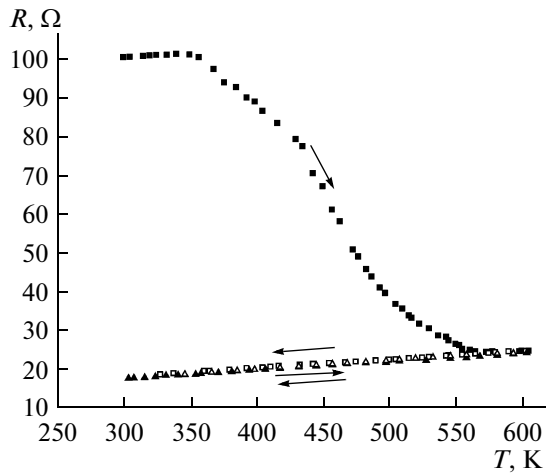


Fig. 5. Variation of the electrical resistivity with temperature during heating and cooling of a layered system consisting of 40 copper films and 40 gold films with the mass thicknesses of 2 nm each.

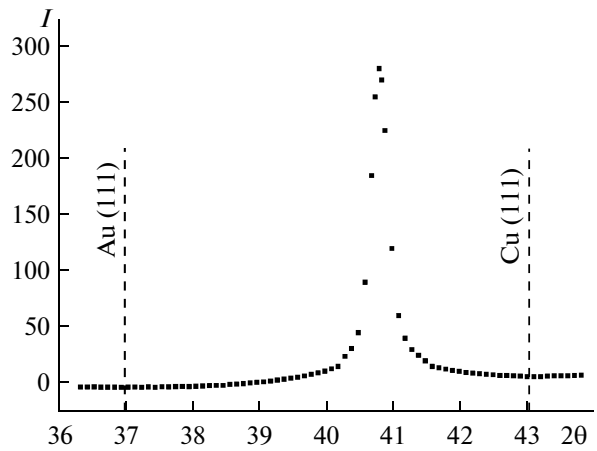


Fig. 6. Diffraction pattern of a layered film system consisting of 40 copper films and 40 gold films with the mass thicknesses of 2 nm each. The pattern was taken after a heating–cooling cycle.

evaluate the energy of activation for the processes involved. Figure 7 shows the decrease in the electrical resistivity upon heating relative to its linear temperature dependence in the $\ln \frac{\Delta R}{R} - 1/T$ coordinates. It is

seen from Fig. 7 that the dependence obtained corresponds to a straight line with an activation energy of 0.43–0.54 eV for the samples with the copper and gold films ~2 nm thick each. This energy should probably be considered as the energy of activation for the homogenization process leading to the formation of a homogeneous alloy from the layered film system; i.e., as the energy of activation of diffusion in such systems. These energy values are in agreement with those [3] found for the vacancy formation in copper and gold nanoparticles (~0.25 eV) if one considers that, with the diffusion being implemented predominantly through the vacancy mechanism, the diffusion activation energy, which is the sum of the vacancy migration and formation energies, is approximately twice as high as the vacancy formation energy.

The relationship between the diffusion coefficients in the layered film system, D , and in macroscopic samples, D_∞ , can be evaluated from the following obvious relationship:

$$\frac{D}{D_\infty} = \exp\left(-\frac{E - E_\infty}{kT}\right).$$

If we use a value $E = 0.5$ eV, which was determined from the variation of the electrical resistivity, and $E_\infty = 1.2$ eV, which is known for macroscopic samples [13], then at $T = 300$ K we have

$$\left(\frac{D}{D_\infty} \approx e^{28} = 10^{12}\right),$$

In other words, the effective coefficient of diffusion in the film system under study at the mass thickness of the Cu and Au films being 2 nm each is 12 orders of magnitude larger than that in bulk samples. Taking the data of the study [12], in which the coefficient of diffusion from copper to gold at 300 K was found to be $D_\infty = 3 \times 10^{-28}$ cm²/s, the effective coefficient of copper diffusion in the layered copper–gold film system under study is $D = 3 \times 10^{-16}$ cm²/s. This agrees with the value calculated above from the electron diffraction data.

This value of the effective diffusion coefficient is also in agreement with the available literature data. For example, it was shown in [6] when studying room-

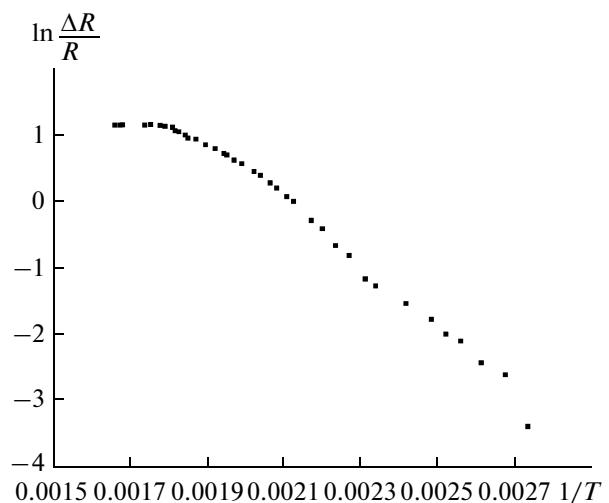


Fig. 7. Temperature dependence of the relative decrease in the electrical resistance of a layered film system during its heating.

temperature gold diffusion into copper samples produced by compaction of nanoparticles ~5 nm in size that the diffusion coefficient was 10^{10} – 10^{12} times larger than the corresponding coefficient for macroscopic samples.

When analyzing experimental results on the size-effect-induced decrease of the melting temperature and of the lattice parameter in fine particles of fcc metals [16], it was shown that in the case of the vacancy mechanism the values of the volume and surface diffusion coefficients in fine particles were much larger than the known values for macroscopic samples. Since the energy of vacancy formation is proportional to the melting temperature, the concentration of vacancies is higher in small-size samples, such as nanoparticles and thin films, whose melting temperature T_r is lower than the melting temperature T_s of bulk samples. Therefore, since the diffusion coefficient of atoms is proportional to the vacancy concentration, the following obvious relationship holds for its dimensional dependence:

$$D = D_\infty \exp\left(-\frac{T_r - T_s E_\infty}{T_s kT}\right).$$

It should be taken into account, in addition, that in the layered film systems with structural elements of a small characteristic size, the diffusion mobility is determined mostly by surface and near-surface vacancies with appropriate energies of formation. It is this factor that is ultimately responsible for such a large increase in the diffusion activity in these nanodispersed film systems.

Thus, the studies undertaken demonstrate that it is the smallness of the characteristic size (small thickness) of the contacting films that plays the decisive role (as compared to the flux of vacancies formed at the condensation front) in the formation of the alloy at the initial stage of condensation of a layered film system.

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