Experimental evidence of a diffusion size effect in thin Au films on Ag(111)

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Abstract. The diffusion size effect, determined by near-surface thin film lattice dynamics, has been experimentally discovered. The investigation was carried out by means of Auger electron spectroscopy enabling determination of the atomic accumulation of the Ag substrate on the (111) surface of the epitaxial Au film. We have shown that the diffusivity $D(x)$ depends upon the distance to the surface x as $D(x) \propto \exp(1/x)$. The size effect characteristic depth was found to be $l \approx 1$ nm for the pair under study.

1. Introduction

Numerous experimental data (see, e.g., [1–3]) show that diffusion in thin films takes place much faster than in bulk solids. Usually this is attributed to a higher density of non-equilibrium defects in thin films. The presence of excess point defects, dislocations and grain boundaries is conditioned by film technology. Therefore the defect densities and, concordantly, the diffusion coefficients may differ considerably as a result of variations in film technology.

It should be noted, however, that the increased defect density is by no means the only cause leading to a diffusion coefficient increase, since diffusion kinetics in thin films are also conditional upon the diffusion size effect. This effect, predicted and studied theoretically [4, 5], must lead to a diffusivity increase with a reduction in film thickness. This is written as

$$D(x)/D = \exp(l/x). \tag{1}$$

Here $D(x)$ is the diffusion coefficient at a distance x from the surface, D is the bulk diffusion coefficient and l is the characteristic depth of the size effect. The diffusion size effect is solely induced by the near-surface crystal lattice dynamics, i.e. the atom mean square displacement in the near-surface zone is larger than in the bulk, as was shown in [5]. It begins to manifest itself below a certain critical thickness.

The characteristic depth of the size effect is

$$l = aAE/kT \tag{2}$$

where a is the lattice parameter, E is diffusion activation energy and

$$A = (2\nu^2 - 3\nu + 3)/8(\nu^2 - \nu + 2). \tag{3}$$

Here $\nu = c_t^2/c_l^2$, where c_t and c_l are the transversal and longitudinal velocities of sound, respectively, in the sample. Our work deals with the detailed experimental study of the dependence of the diffusion coefficient on the single-crystal film thickness.

It should be noted that, in thin films, at least two other size effects may be observed:

(i) the size effect induced by the presence of traps in the diffusion zone, which manifests itself when the distance between traps is less than the film thickness [6];

(ii) the size effect induced by the statistical nature of diffusion which shows in the fractal roughness of the diffusion front [7].

The study of these effects is not the object of the present work.

Up to now there has been no reliable experimental proof of the diffusion size effect. This paper is intended to reveal and investigate this effect. In this respect, the Au/Ag system is one of the most favourable, owing to its outstanding simplicity. Here both components are fully miscible, and lattice parameters are almost identical; therefore no problems of phase formation and misfit accommodation arise. Furthermore, it has been demonstrated in detail [8–11] that nearly perfectly epitaxial Au films on Ag crystals can be prepared, which have a uniform film thickness and negligible amount of volume defects. Hence problems arising from film roughness and short-circuit diffusion within defect-induced paths can be ignored.

The corresponding experiments were performed by AES and TEM. The time dependence of the Ag-to-Au Auger signal intensity ratio during annealing of gold films on silver substrates was studied. The data found were analysed with a stepwise data-fitting procedure.

2. Experimental details

The Au/Ag thin film/substrate diffusion couples were prepared using electrolytically grown Ag crystals as substrates, whose preparation has been described elsewhere [8]. The deposition of the Au films and the diffusion experiments were performed in an UHV apparatus (base pressure, 10^{-8} Pa), equipped with AES, an Ar ion gun and evaporation sources for Au and Ag. The Ag crystals were cleaned *in situ* by Ar ion etching ($2\ \mu A\ cm^{-2}$; 600 eV), followed by annealing at 670 K for 1 h for full crystal restoration. The films were deposited mainly at room temperature on the (111) faces of the Ag crystals at a rate of about 1 monolayer (ML) min^{-1}. (The thickness of 1 atomic ML is 0.2357 nm.) For evaluation of the size effect the thickness of the films ranged between 5 and 12 ML. The thickness was measured by means of a calibrated quartz oscillator with an error of about 3%.

In the diffusion experiments the samples were isothermally annealed at temperatures between 497 and 510 K. The temperatures were measured with a calibrated Ni–Cr–Ni thermocouple welded to the Ag crystals and stabilized to within -0.5 K by a regulation system. During annealing, the study of diffusion-induced changes in the surface composition was performed by AES. After diffusion the alloyed films were removed by Ar

ion sputtering. Another Au film was deposited on the newly cleaned and annealed Ag crystals, thus enabling the subsequent diffusion experiments to be carried out. For comparison, the experiments were correlated with diffusion studies performed on the same equipment with thicker Au films on Ag (the Au film thicknesses were between 20 and 100 ML), where the size effect influence was negligible. These investigations, whose results have been described elsewhere [12], were based also on the concentration–depth profiles obtained by a combination of Ar$^+$ sputter sectioning and AES.

AES analysis was performed by means of a CMA with normally impinging primary electrons with 2 kV energy, a 15 μA beam current and an approximately 0.3 mm beam diameter. The AES spectra were taken in differentiated mode with a modulation voltage of 2 V peak to peak. In the spectra, mainly the AES signals of Au and Ag at 69 eV and 356 eV, respectively, were analysed. The peak-to-peak signal amplitudes were assumed to be proportional to the Auger electron intensity.

In connection with the considerably complicated diffusion picture the application of ion sputter etching to depth–profile concentration measurement was rather problematic in the present work. Therefore the accumulation rate of the diffusant on the Au surface was used.

The experiments were complemented by TEM investigations of Au film micro-morphology and perfection. To this end the films were stripped electrolytically from the Ag substrates.

3. Main characteristics of the Au/Ag diffusion couples

3.1. Crystalline perfection

TEM analysis has shown that thin Au films on Ag(111) substrates have a high degree of epitaxial perfection. Because of the small misfit (about 0.2%) the film formation pro-ceeds pseudomorphically [13]. Only a few twins or stacking faults due to double posi-tioning have been locally identified [13]. They were annealed, however, at temperatures below 470 K. Moreover, some screw dislocations—obviously induced by screw dis-locations ingrown in the Ag substrate crystals [9]—were observed (density, about 10^{-8} cm^{-2}). Owing to this relatively high degree of film perfection, defect-induced short-circuit diffusion and grain boundary diffusion can be neglected. Also pipe diffusion induced by dislocations is negligible since the film thickness, which is roughly equal to the diffusion width, is almost three orders of magnitude smaller than the mean distance between dislocations. The diffusion process may thus be attributed only to pure volume diffusion, resulting from the vacancy mechanism, as in other FCC metals.

3.2. Interface and surface roughness

The (111) surface of the Ag substrate crystals are almost atomically smooth. Indirect TEM imaging revealed a mean distance of atomic surface steps of some 10^{-1} μm [8]. During room-temperature deposition of Au, volume diffusion effects are negligible [10, 12]. Thus, the diffusion samples initially had ideally definite and sharp interfaces.

On the smooth Ag substrates, Au grows via repeated 2D nucleation, resulting in the formation of atomically stepped hillocks [9], which induces some film surface roughness. These hillocks, however, are completely smoothed by surface diffusion during annealing, even at temperatures below 470 K [12], where volume diffusion is still ineffec-tive [10]. Only a few 2D islands and 2D pits with monoatomic thickness are left on the Au
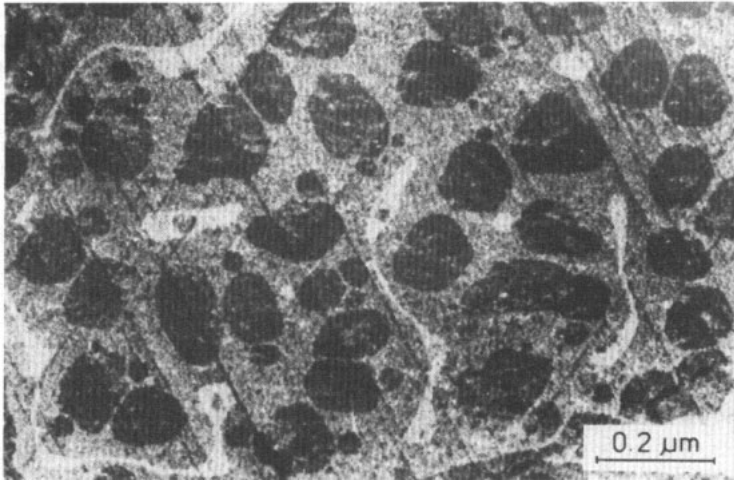
Figure 1. TEM microphotograph of a Au film on Ag(111) taken after annealing at 443 K (annealing time, 4.5 h; mean film thickness, 5.9 ML; extinction constrast). During annealing, the surface roughness disappears completely. Only some 2D islands (darker areas) or 2D pits (lighter areas) remain.

film surface (figure 1) and a uniform film thickness can always be assumed, which essentially simplifies the analysis of the experimental results. Below a mean film thickness of nearly 5 ML, owing to the hillock growth the Au films do not cover the Ag substrate entirely.

3.3. Surface segregation

The analysis of the films alloyed by diffusion revealed that Ag is enriched in the topmost atomic layer, owing to its lower surface energy. In order to take this effect into account, the surface compositions of homogeneous Au–Ag alloys were studied systematically for different volume concentrations. Thicker Au–Ag alloy films (film thickness above 50 ML) were used as samples, prepared by codeposition of Au and Ag onto Ag crystals. The main results on the segregation are shown in figure 2.

3.4. Volume diffusion parameters

Special diffusion studies [12] performed to analyse low-temperature diffusion in thicker Au films revealed no indications of size effects for Au film thicknesses above 20 ML. A strong concentration dependence of the diffusion coefficient was observed for the temperature range considered (536–659 K):

$$D(c_v^{Ag})/D(c_v^{Ag} = 0) = 0.8 \exp(-4.5c_v^{Ag}) - 0.1989c_v^{Ag} - 0.2 \qquad (4)$$

with c_v^{Ag} being the Ag concentration.

The temperature dependence of D follows the Arrhenius law

$$D(c_v^{Ag} = 0) = 0.025 \exp[-(1.62 \text{ eV})/kT] \qquad (5)$$

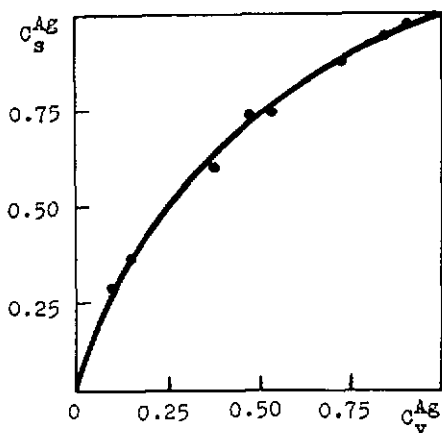where k is Boltzmann's constant and T is the absolute temperature.

Figure 2. Dependence of the Ag concentration c_s^{Ag} of topmost atomic surface layer of homogeneous Au–Ag(111) alloys determined at temperatures of around 573 K on the volume concentration c_v^{Ag}.

The activation energy measured is about 7% smaller than that determined in conventional diffusion studies at higher temperatures, i.e. at temperatures between 1000 and 1300 K [12]. This means that, unlike the high-temperature range where vacancy complexes (dimers, trimers and so on) are also involved [14], in the low-temperature range there occurs a pure monovacancy diffusion.

3.5. Contribution of gradient energy

When studying diffusion in very thin films, the influence of gradient energy should be taken into consideration. This can be done using equations (5) and (6) in [15], taking $\lambda = 2d$. Considering only the first term of the series $B^2(\lambda)$ the diffusion coefficient is expressed as

$$\tilde{D}(d) \simeq D[1 - (2H/f'')(\pi^2/d^2)]. \tag{6}$$

Here H is the gradient energy factor and f'' is the second-order derivative of the free energy in the alloy with respect to concentration.

For Au/Ag systems, $H/f'' \simeq -4.5 \times 10^{-17} \text{ cm}^2$ [15]. It is obvious that, even for the thinnest (5 ML) Au film studied, the correction factor is small and does not exceed 5%, and so we have neglected it in further calculation.

4. Simulation of diffusion kinetics

For theoretical modelling of thin-film diffusion kinetics the size, concentration, segregation, temperature and time dependences must be taken into account, and defect-induced diffusion effects may be neglected.

Let us suppose, as has been done in [11], that segregation results in an increase in the concentration of the diffusant (in our case Ag) only within the first atomic layer of the crystal. In [11] a detailed study is given of the $c_v(c_s)$ dependence, characterizing the degree of segregation in the Au–Ag alloy (c_s and c_v are the surface and bulk concentrations, respectively, of the diffusant). The dependence is shown in figure 2.

Let us solve the diffusion equations numerically by the finite-difference method at the reflecting boundaries. The boundary conditions in our case are dictated by the fact that during our experiment the diffusion flow through both free surfaces is equal to zero. In our case the diffusion coefficient depends on both the coordinate and the concentration. The concentration dependence of the diffusivity for any temperature is given by equations (4) and (5). Thus, the diffusion coefficient can be written as

$$D(x, c) = D(x)D(c). \tag{7}$$

Here the first cofactor is taking from (1), and the second provides the concentration (4) and temperature (5) dependence. The diffusion equation can thus be written as the relationship

$$\partial c / \partial t = (\partial / \partial x)[D(x, c)\, \partial c / \partial x]. \tag{8}$$

It is necessary to take correctly into account the effect of segregation on diffusion in thin films, when analysing the diffusion process kinetics according to experimental data on the accumulation rate of diffusant on the surface. Here the difficulty lies in the fact that in thin films the amount of material removed (eliminated) from the diffusion process as the result of segregation on the surface is comparable with the whole amount of diffused material. This means that segregation in thin films leads to a corresponding decrease in the volume concentration of the diffusant in the near-surface region. Without solving this problem it is impossible to analyse correctly the diffusion processes in thin films from the viewpoint both of the concentration pattern and of the kinetics of the accumulation of diffusant on the film surface. As far as know, this problem has not yet been solved. We have developed a procedure of numerical analysis of diffusion processes in thin films when segregation is present.

Our procedure of diffusion analysis in films with segregation present proceeds from the concept that at each time step of the numerical count the diffusion system 'feels' not the real but the effective Ag concentration in the first atomic layer. This effective concentration is less than the real concentration, which corresponds to the real process since, owing to segregation, some of the Ag atoms from the first layer are removed from the diffusion process as they 'stick' to the surface.

Knowing the $c_v(c_s)$ dependence [11], for a given real Ag concentration c_0 on the surface it is possible to determine its effective concentration on the surface $c_s^{\text{eff}} = c_v(c_s = c_0)$. Indeed, if the Ag bulk concentration and real concentration on the surface were c_s^{eff} and c_0, respectively, there would have been no diffusion flow. This means indeed that, when the real Ag concentration on the surface is c_0, its effective (for diffusion) concentration on the surface is c_s^{eff}.

Let us suppose that after the first time step the silver concentration within the first layer is $c(1, 1)$. We substitute this quantity by the effective concentration value $c_s^{\text{eff}} = c_v (c_s = c(1, 1))$. Now, during the second time step the atoms of the second and subsequent atomic layers diffuse as if the Ag concentration in the first layer was less than it is in reality, that is as if it was equal to c_s^{eff}. This results in an increase in the diffusion flow of Ag atoms to the first layer compared with the case when segregation is absent. After the second step we compute the amount c of Ag diffused into the first layer, and this gives us the real Ag concentration within the first layer: $c(1, 2) = c(1, 1) + \Delta c$. Prior to the third step this quantity is substituted by $c_s^{\text{eff}} = c_v (c_0 = c(1, 2))$ and so on.

Thus, for each instant of time both the real and the effective (for diffusion and thermodynamic equilibrium) concentrations of Ag atoms in the first layer were determined, as well as their concentrations within all the layers.

Further, since for each depth of diffusion size effect the dependence $c(x, t)$ was known, we determined the kinetics of the increase in Auger electron current.

5. AES analysis

To calculate the AES data for the assumed concentration models, a semiempirical relation was used, derived from the sum of the contributions of each ML parallel to the surface to the total AES signal. To reduce errors in the measured intensity, induced by slight shifts of the analysing system, the Auger intensity ratios I^{Ag}/I^{Au} of Au to Ag were considered. As was shown in [10],

$$\frac{I^{Ag}}{I^{Au}} = 3.57 \sum_{n=1}^{\infty} c_n^{Ag} w_n^{Ag} \bigg/ \sum_{n=1}^{\infty} (1 - c_n^{Ag}) w_n^{Au} \tag{9}$$

where c_n^{Ag} and c_n^{Au} are the concentrations of Ag and Au in the nth atomic ML, the topmost having $n = 1$, and w_n^{Ag} and w_n^{Au} are the normalized contributions of the nth layer to the total intensity, for a homogeneous contribution. The quantities w_n^{Ag} and w_n^{Au} were obtained in [9].

6. Experimental results and discussion

The experimental investigation of Auger signal changes in Au and Ag has yielded data characterizing the kinetics of Ag accumulation growth on the Au film surface during annealing.

For each experimental dependence of the Auger electron intensities the corresponding theoretical dependence on the factor A (see equation (2)) chosen was plotted so as to provide the best fit with the experimental data, i.e. to provide coincidence (within experimental error) of the theoretical and experimental values of the Auger electron current intensities at half the annealing time. The experimental data graphs and theoretical graphs optimally matching experimental data are shown in figure 3.

For each of three experiments we also determined the sensitivity of the factor A to measurement errors of the annealing temperature ($A_T' = \partial A/\partial T$) and film thickness ($A_d' = \partial A/\partial d$), which contributed most to the total error in determining the factor A. The total error was evaluated as

$$A = A_T' \Delta T + A_d' \Delta d \tag{10}$$

where ΔT and Δd are the errors in determination of the film annealing temperature and film thickness, respectively. We assumed the $\Delta T = 1$ K and $\Delta d = 0.03d$ (see section 2). The corresponding values of A, A_T', A_d' and ΔA are listed in table 1.

The analysis of the experimental data provides for the factor A a value of 0.063 ± 0.020. This means that, by way of example, for an annealing temperature of 500 K the size effect depth in our system is (see equation (2)) $l = 1.0 \pm 0.3$ nm.

We shall now determine the theoretical value of the diffusion size effect depth in the investigated system. We shall first compute the theoretical value of the factor A. Taking $\nu^{Au} = 0.137$ and $\nu^{Ag} = 0.195$ we find from equation (3) that $A^{Au} = 0.174$ and $A^{Ag} = 0.176$. Since the bulk activation energy $E = 1.62$ eV and the lattice constant $a = 0.4078$ nm, equation (2) yields the theoretical value of the diffusion size effect depth in the system under study; for a temperature of 500 K it is $l = 2.7$ nm.
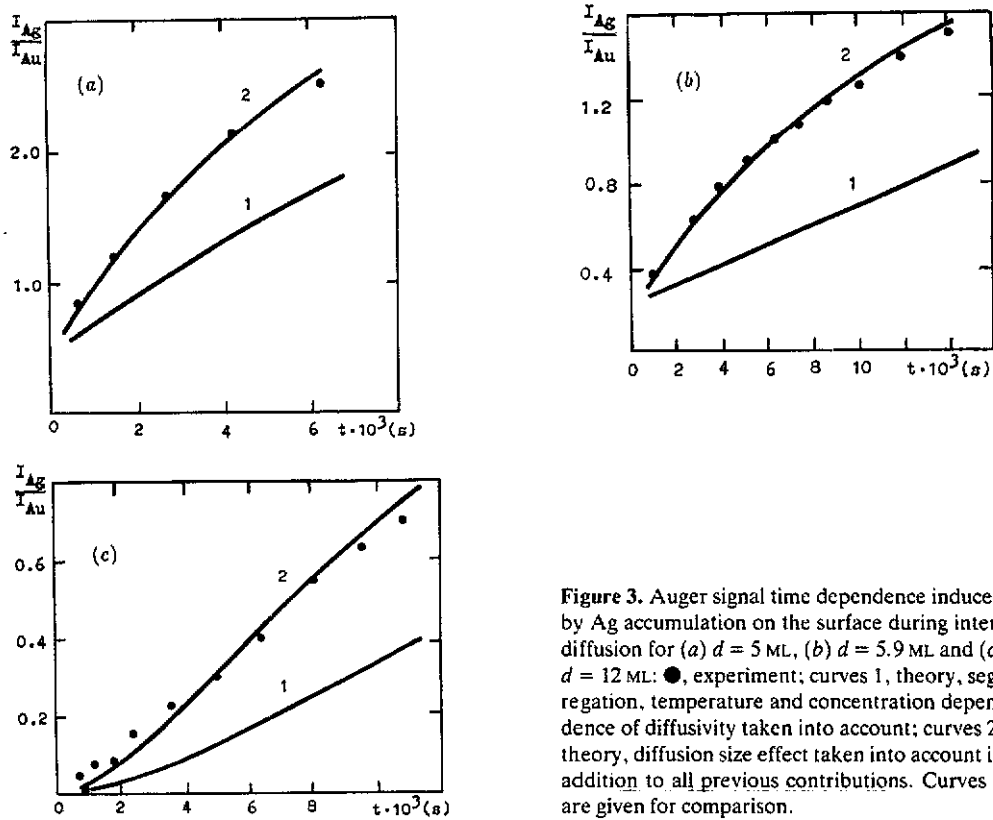
Figure 3. Auger signal time dependence induced by Ag accumulation on the surface during interdiffusion for (a) $d = 5$ ML, (b) $d = 5.9$ ML and (c) $d = 12$ ML: ●, experiment; curves 1, theory, segregation, temperature and concentration dependence of diffusivity taken into account; curves 2, theory, diffusion size effect taken into account in addition to all previous contributions. Curves 1 are given for comparison.

Table 1. Size effect characteristics for an Au film on the surface (111) of an Ag single crystal.

Film thickness (ML)	Annealing temperature (K)	Factor A value	Sensitivity		Factor A error ΔA
			A_T'	A_d'	
5.0	510	0.050	0.005	0.2	0.011
5.9	497	0.068	0.005	0.2	0.011
12.0	508	0.070	0.009	0.3	0.018

Thus, the theoretical value of the diffusion size effect is 2.7 times greater than the experimental value. Such a discrepancy may be considered not too large, taking into account that, when equations (1) and (2) were being deduced, use was made of the high-temperature approximation and of the elastic continuum model. Perhaps, surface relaxation contributes to the discrepancy, although it is difficult to expect that the relaxation affects diffusion in a film 12 ML thick because it results in atomic displacements by a few per cent even in the first ML [16, 17]. Also, it should be supposed that the experimental value of the factor A will be different for other crystallographic orientations of the free surface.

In the experiment performed, we investigated the use of a strong film–substrate bond. It is obvious that for a weak film–substrate bond the size effect will manifest itself

more intensely. If the bond with the substrate is so weak that both film surfaces can be considered free, as was shown by two of the present authors [5], the diffusion size effect is expressed as $D(x)/D = \exp[l/x + l/(d - x)]$. In the middle of the film the diffusion coefficient is minimal: $D(d/2) = D \exp(4l/d)$. For instance, for a free Au film, considering the value experimentally obtained here for the size effect depth $l = 1$ nm, the thickness dependence of the diffusion coefficient in the middle of the film is expressed as $D(d/2) = D \exp(4nm/d)$.

7. Conclusions

The principal results of this work are as follows.

   (i) The salient features of the predicted diffusion size effect induced by near-surface dynamics were experimentally confirmed.
   (ii) An original method to account for the surface segregation effect upon diffusion was proposed.
   (iii) The characteristic depth of the diffusion size effect for accumulation of Ag substrate atoms on Au epitaxial film was found to be 1 nm.

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