

Experimental evidence for a nonparabolic nanoscale interface shift during the dissolution of Ni into bulk Au(111)

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We report experimental evidence for the violation of the “diffusional parabolic law” ($x \propto t^{0.5}$, where x is the interface shift and t is time) as predicted recently by computer simulation [Z. Erdélyi *et al.*, Phys. Rev. B **69**, 113407 (2004)] for a binary system with restricted mutual solubility. Using x-ray photoelectron spectroscopy we investigated the shift of the interface between a thin Ni layer (3 nm) deposited under UHV conditions on top of a Au(111) single crystal during its thermally driven dissolution into the Au substrate. From the temporal evolution of the Ni-2*p* and Au-4*f* core level intensities at various fixed temperatures, a power law could be extracted for the time dependence of the interface shift ($\propto t^{k_c}$) with exponents in the range of 0.6–0.7. Thus, clear experimental evidence is provided that the kinetics of such a shift might differ from the well known parabolic law if restricted to the nanometer scale.

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I. INTRODUCTION

Studies of diffusional movement of atoms through interfaces and of the resulting interface shift are nowadays of great interest not only from a fundamental research point of view—search of diffusion laws valid on the nanoscale—but they are of practical importance as well. Recent progress in device technology allows one to directly approach structures on the nanoscale, for which the knowledge of the corresponding diffusion laws is indispensable. Also related to this topic is the possible degradation of parts of electronic devices being often due to material transport through interfaces. Accordingly, in order to extend the lifetime of such devices a detailed picture of the underlying diffusional processes is required.

During the past years several papers were published about the interface motion during thin film dissolution into semi-infinite substrates.^{1–4} Recently, both computer simulations and experiments on the Ni dissolution into a Cu substrate⁴ gave first hints for nonclassical diffusion by revealing that the interface shift in this completely mutual soluble system evolves linearly in time. The simulations additionally indicated⁴ that this deviation from the classical parabolic law is restricted to the nanoscale: with increasing time or, alternatively expressed, for shifts exceeding approximately 10 nm, the system gradually turns back to classical diffusion.

A similar behavior has been predicted recently⁵ from calculations for phase separating systems in contrast to earlier simulations^{1–3} where, neglecting the composition dependence of the diffusivity (diffusion asymmetry), a parabolic law had been obtained. In the present contribution—in accordance with theoretical prediction⁵—clear experimental evidence will be provided for a nonparabolic shift ($x \propto t^{k_c}$, where $k_c > 0.5$) of an initially steplike interface in a nonmiscible binary system.

It is important to note that there are numerous examples of experimentally observed nonparabolic growth kinetics in

the literature. However, in all of these cases the linear growth of phase(s) in solid state reactions was interpreted as a consequence of the reaction rate control at the interface(s).^{6–9}

The deviation from the parabolic law in our case has pure diffusional origin and, for a given *A-B* system of restricted mutual solubility, depends on two parameters: (i) the strength of the composition dependence of the diffusion coefficient parametrized here by m' , which gives the difference between the diffusion coefficients in pure *A* and *B* matrixes in orders of magnitude and (ii) the parameter characterizing the phase separation tendency V/kT (V is the mixing energy or regular solution parameter,^{5,10} which measures the phase separating or ordering strength, k is the Boltzmann constant, and T the absolute temperature). As has been shown in Ref. 5, for small values of V/kT the kinetic exponent k_c can even approach one for increasing m' , while this deviation from classical behavior decreases with increasing V/kT .

In order to prove a nonparabolic behavior experimentally, the Ni-Au system is a good candidate, since it has limited mutual solubility [$\approx 3\%$ at about 680 K, $V=0.019$ eV (Ref. 11)]. Additionally, it can be estimated for the temperatures investigated (643–733 K, i.e., $V/kT=0.343–0.301$), that the diffusion of Ni in Au is about 6 orders of magnitude faster¹² than the corresponding self-diffusion making $m' \approx 6$. To measure the interface shift, a similar experimental setup was chosen as in Ref. 4: a thin [≈ 13 monolayers (ML) thick] Ni film is deposited onto the Au(111) single crystalline substrate under ultrahigh vacuum (UHV) conditions and the time dependence of the Ni and Au XPS intensities is determined during controlled heat treatments.

II. EXPERIMENTAL

The measurements were carried out in a multichamber UHV system at a base pressure $< 10^{-10}$ mbar, equipped with XPS, ultraviolet photoelectron spectroscopy (UPS), scanning

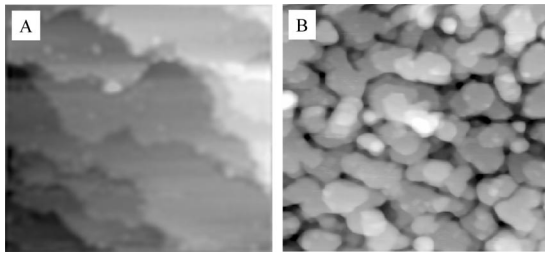


FIG. 1. STM images of the Au single crystal surface before (A: $46 \times 46 \text{ nm}^2$, z scale 2.8 nm) and after (B: $46 \times 46 \text{ nm}^2$, z scale 2.3 nm) deposition of 3 nm Ni.

tunneling microscopy (STM), low-energy electron diffraction (LEED), and evaporation facilities (Omicron EFTM-3). The XPS/UPS system is equipped with a 100 mm hemispherical electron analyzer, a $\text{Mg-K}\alpha$ x-ray source for XPS and a He discharge lamp (He-I, 21.2 eV was used) for UPS measurements. The Ni/Au(111) samples were prepared using a commercial gold single crystal with a miscut of $< 2^\circ$. The Au crystal was cleaned and its surface quality improved *in situ* prior to the nickel deposition by applying repeated cycles of 1 keV Ar^+ bombardments and annealing at 973 K with the temperature determined by a pyrometer. As demonstrated by STM [Fig. 1(A)] after the above cycles, a clean Au(111) surface with approximately 10 nm wide terraces was obtained. This terrace width corresponds well to the miscut of the crystal. The surface quality and orientation has also been checked by LEED. XPS analysis was finally used to prove the cleanliness of the sample surface after the various preparation steps.

After these pretreatments, a 3 nm thick (approximately 13 ML) Ni film was evaporated at room temperature onto the Au(111) surface at a deposition rate of 1 nm/min. The film quality could be checked by STM [Fig. 1(B)] UPS, XPS, and LEED allowing the conclusion that closed, textured nanocrystalline Ni layers were obtained with grains preferentially oriented in (111) direction and a lateral size of $d \approx 10 \text{ nm}$.

Figure 2 presents the corresponding UPS spectrum of the clean Au surface (bottom curve) and that after Ni deposition (top curve). The latter exclusively shows features originating from Ni if compared to a Ni reference sample (not shown here). Therefore, taking into account the sampling depth of the UPS experiment ($\approx 2 \text{ ML}$), the completely missing Au signal after Ni evaporation unequivocally proves that this 3 nm Ni film is closed. In addition, several UPS spectra were acquired to analyze the near surface region (2 ML) during annealing. Since gold atoms have the tendency to segregate on the top of Ni (Ref. 13) and the evaporated Ni film is nanocrystalline, a fast appearance of Au on the surface is expected due to short circuit diffusion along the twist grain boundaries. Such a behavior can indeed be observed in Fig. 2, where the temporal evolution of the UPS valence band spectrum is also presented at 673 K. After a short annealing time of 13 min (during which no significant interface shift is expected) a fast decrease of the Ni-3d band intensity, accompanied by an equally fast increase of the Au-5d band signal, is observed. Even after a long term heat treatment (250 min) traces of the Ni-3d band can still be observed as compared to

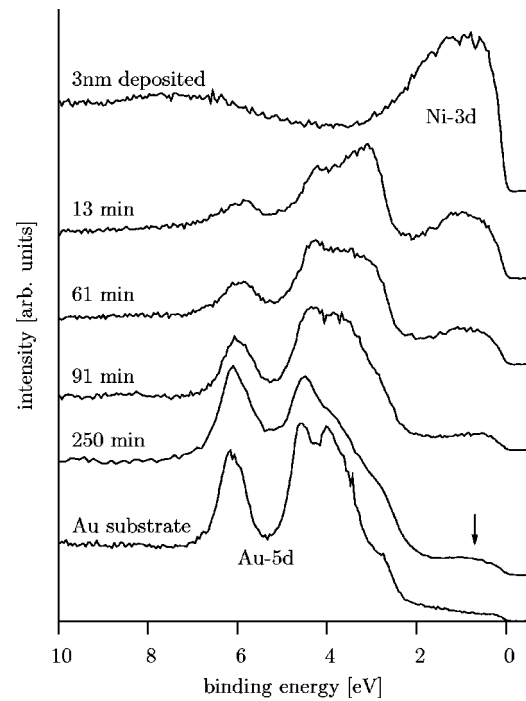


FIG. 2. UPS (He-I) spectra before (bottom curve) and after Ni deposition (top curve) together with results showing the time evolution during heat treatment at 673 K.

pure Au (see arrow). This gives clear evidence for saturation behavior of the segregation process which finally results in a Au film thickness which does not significantly exceed the information depth of the UPS technique ($\approx 2 \text{ ML}$).

In order to investigate the shift of the Ni/Au(111) interface, the sample was heat treated at temperatures between 643 and 733 K. During annealing XPS spectra of the Au-4f and Ni-2p levels were repeatedly taken in intervals of two minutes, the time needed to acquire both spectra.

The XPS results are presented in Fig. 3 where the ratio of the integrated Au-4f and Ni-2p core line intensities is given as function of the annealing time. This ratio is expected to increase with time for both processes, i.e., for segregation of

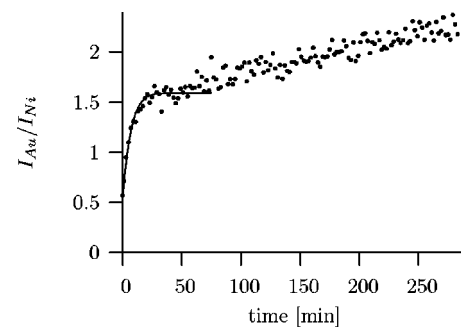


FIG. 3. Time evolution of the ratio between the Au-4f and the Ni-2p core line intensities measured at $T = 643 \text{ K}$ (dots). The sudden increase at the beginning is due to the fast grain-boundary diffusion and segregation of Au on top of the Ni surface. The solid line represents the fit of the first time domain (Hwang-Balluffi type) combining Eqs. (1) and (2) and using the initial thickness of the deposited Ni layer, as described later in the text.

Au atoms on top of the Ni film as well as for dissolution of Ni atoms into the Au single crystal, respectively. Obviously, a monotonous increase can indeed be recognized in Fig. 3. However, there clearly exist two different time domains indicating a fast change of this ratio at the beginning (up to about 60 min) and a slow, but still monotonous increase for longer times. While the first can easily be identified as being due to the fast segregation of Au mentioned before, the latter reflects the interface shift during the dissolution of Ni atoms into the Au single crystal.

This dissolution can not be traced by the UPS experiment because of the very limited information depth (2 ML). For XPS, on the other hand, the sampling depth of about 2 nm is much larger due to the significantly increased kinetic energy of the outgoing photoelectrons. At first sight, this value might seem to be too small, as compared to the thickness of the as-prepared Ni film of 3 nm, to allow Au atoms from the buried Au single crystal to contribute to the measured spectra. However, in the present case, there is a damping of the photoelectron intensity emitted from the Au substrate by only a factor of $\exp(-3 \text{ nm}/2 \text{ nm}) \approx 5$ due to the Ni top layer. Such a reduction still allows the collection of statistically well-defined data with reasonable effort, especially due to the very narrow intrinsic line width [Au-4f: 0.3 eV full width at half maximum (FWHM)] as compared to the Ni intensity (Ni-2p: 1.5 eV FWHM). The above intensity estimate is confirmed by closer inspection of Fig. 3 where a well detectable Au signal can be recognized at $t=0$. Therefore, it can be safely assumed that the thickness of the Ni film and, thus, the shift of the interface between the Au substrate and the Ni layer can be reliably studied by means of a proper analysis of the XPS results given in Fig. 3.

III. ANALYSIS OF THE EXPERIMENTAL DATA

In order to arrive at a quantitative picture, the results given in Fig. 3 have been analyzed taking into account not only the shift of the Ni/Au(111) interface but also the fast Au grain-boundary diffusion leading to surface saturation and to the formation of an ultrathin Au layer on top of the Ni surface. For this purpose the model sketched in Fig. 4 has been used assuming that the surface is asymptotically covered with 1–2 ML of Au during the very first stage of the heat treatment.

Denoting the time dependent thickness of the segregated Au top layer by n^* and that of the evaporated Ni layer by n , respectively (both expressed as equivalent monolayers), these quantities can be extracted from the measured XPS intensity ratios as reported previously in Refs. 4 and 14:

$$\frac{I_{\text{Ni}}}{I_{\text{Au}}} = \frac{(\alpha_{\text{Ni}}^{\text{Au}})^n [1 - (\alpha_{\text{Ni}}^{\text{Ni}})^n]}{(\alpha_{\text{Au}}^{\text{Au}})^{n^*} (\alpha_{\text{Au}}^{\text{Ni}})^n + 1 - (\alpha_{\text{Au}}^{\text{Au}})^{n^*}} S. \quad (1)$$

Here α_B^A is the attenuation coefficient for photoelectrons from B atoms in matrix A , and S is the relative sensitivity factor, which can be obtained from reference XPS measurements on Au and Ni bulk samples.

Since the present Au segregation and saturation through the nanocrystalline Ni film—occurring at the early stage of

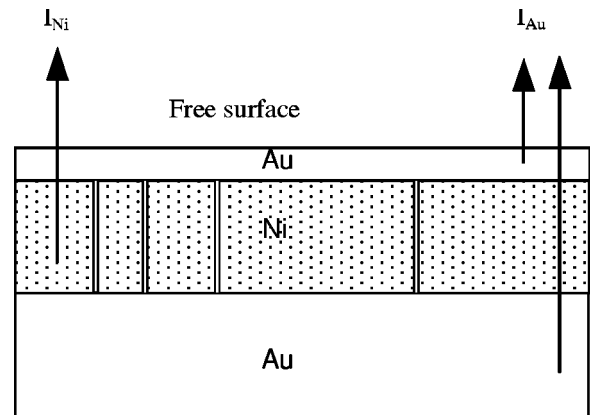


FIG. 4. The model used for analysis of the XPS data. The surface is asymptotically covered with 1–2 ML of Au during the very first stage of the heat treatment. The arrows represent the XPS signals from the different parts of the sample.

the time development—is in complete analogy to the classical Hwang-Balluffi-type experiment on grain-boundary diffusion,^{15,16} it is plausible to assume a corresponding exponential time dependence for the growing Au top layer:

$$n^*(t) = n_{\infty}^{\text{Au}} [1 - \exp(-\omega t)]. \quad (2)$$

Here

$$\omega = \frac{2\delta D_b s_b}{N_{\infty}^{\text{Au}} N_0^{\text{Ni}} s_s d}, \quad (3)$$

where $\delta=0.5$ nm is the grain-boundary width, s_b and s_s are the grain-boundary and surface segregation factors, respectively, N_{∞}^{Au} and N_0^{Ni} are the Au and Ni thicknesses in nanometer respectively, and D_b is the grain-boundary diffusion coefficient.

Furthermore, the shift of the Ni/Au(111) interface is described by a power law in time similarly to the computer simulations given in Ref. 5:

$$n(t) = n_0^{\text{Ni}} - vt^{k_c}. \quad (4)$$

Using Eq. (1) for the XPS intensities obtained after deposition we can calculate the initial thickness of the deposited Ni layer (n_0^{Ni}) using $n^*=0$ (the thickness of the segregated Au layer is 0).

Combining Eqs. (1) and (2) and using the previously obtained initial thickness of the deposited Ni layer as a fixed value for the Ni thickness n it is possible to calculate the final thickness of the segregated Au layer (n_{∞}^{Au}) (which can be used to check the reliability of the fit by comparing to the experimental UPS result) as well as the corresponding ω from the first time domain of the process (which corresponds to the segregation of Au on top of Ni).

Using this n_{∞}^{Au} value obtained from the above analysis as a fixed value for the segregated Au thickness (n^*) we can calculate the thickness of the buried Ni layer as a function of time in the second time regime. Thus, according to Eq. (4) it is plausible to fit the $\log_{10}[n_0^{\text{Ni}} - n(t)]$ vs $\log_{10}t$ plot with a linear function. This way the slope of the plot will give the value of k_c .

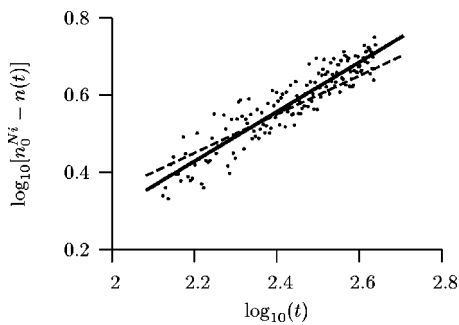


FIG. 5. Plot of the logarithm of the interface shift vs logarithm of time for 643 K. The solid line represents a linear fit. Its slope gives $k_c=0.64$, the kinetic exponent. The dashed line corresponds to a line with a slope of 0.5.

IV. RESULTS AND DISCUSSION

Figure 3 shows the result of the fit (solid line) of the first time domain (corresponding to the Au segregation and saturation process) for 643 K using $n_0^{\text{Ni}}=13.5$. The fit yields $n_\infty^{\text{Au}}=1.3$ ML and $\omega=2 \times 10^{-3} \text{ s}^{-1}$. Since in a Hwang-Balluffi type experiment the surface coverage is usually 1–2 ML, the value for the final Au thickness (1.3 ML) indeed confirms the reliability of the fit, and is in agreement with the thickness deduced from UPS measurements. From ω and the values of all the parameters in Eq. (3), one can calculate $D_b s_b / s_s$, arriving at $2 \times 10^{-20} \text{ m}^2 \text{ s}^{-1}$ at 643 K. Moreover, for Ni diffusion via Ni twist grain boundaries the value of D_b is known to be $1.35 \times 10^{-19} \text{ m}^2 \text{ s}^{-1}$ from literature.¹² Considering that s_b / s_s is certainly less than 1, but very likely higher than 0.1, the above value for ω is really satisfying.

Figure 5 shows the $\log_{10}[n_0^{\text{Ni}} - n(t)]$ vs $\log_{10}t$ plot for 643 K in order to determine the kinetic exponent (k_c). The solid line represents the fit to the plot and yields $k_c=0.64$. Additionally a line with a slope of 0.5 (dashed line) is also presented to show the deviation from the parabolic behavior.

Figure 6 finally presents the values for the kinetic exponents k_c as determined experimentally along the route described above together with corresponding computer simulations⁵ for different m' values. From this plot, the main result of this work can clearly be seen: The experimental data of k_c are significantly higher than 0.5 providing convincing evidence for the predicted deviation of the diffusional interface shift from classical behavior. One step further, even

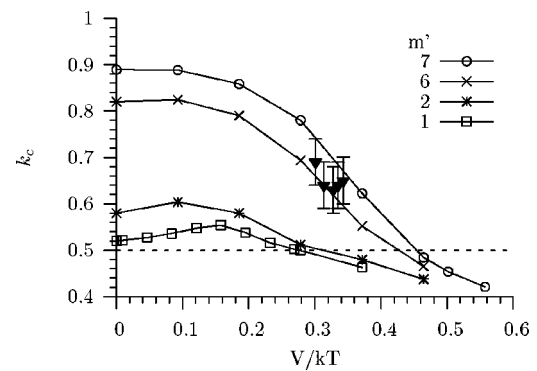


FIG. 6. Kinetic exponents k_c versus V/kT for different m' values as simulated in Ref. 5. The solid lines connect the simulated results as a guide to the eye. The experimentally determined data are inserted as solid triangles (\blacktriangledown) including error bars representing the uncertainty of the parameter fit. Since for Au-Ni, experiments suggest a value of $m' \approx 6$ within the investigated temperature range together with $V=0.019$ eV, excellent agreement between simulation and experiment is found. The classical diffusion behavior is indicated by the horizontal dashed line.

quantitative agreement between simulation and experiment is found within the limits set by the accuracy of the data for V and m' as well as the uncertainty of the parameter fit.

We must note, that in general k_c is time dependent,⁵ but within our time window the change of the Ni thickness was only about 5–6 ML (initial thickness of Ni ≈ 13 ML), making this time dependence unobservable.

In conclusion, following the temporal evolution of XPS signals during the dissolution of a thin Ni deposit into a Au(111) single crystalline substrate, we have demonstrated that the diffusional shift of a chemically sharp interface can deviate from the classical parabolic law ($t^{0.5}$) changing into a more general power law $x \propto t^{k_c}$ with $k_c \approx 0.6-0.7$. This deviation is found to be in very good agreement with predictions based on recent computer simulations.⁵

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