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The Surface Composition of the Gold-Palladium Binary Alloy System

by

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ABSTRACT

The surface composition of the AuPd alloy system has been determined by Auger Electron Spectroscopy. Measurements were performed on polished polycrystalline alloy foils. After cleaning, the intensities of the 71 eV and 2024 eV gold Auger transitions, and the intensity of the 330 eV palladium transition were measured, and then converted to atom concentrations in the surface layer. The surfaces of the annealed samples were found to be significantly enriched in gold with respect to the bulk. This result disagrees with the regular solution theory prediction. After extensive sputtering of the AuPd alloys with 1.5 keV Ar⁺ ions, a slight surface enrichment with palladium was found, as predicted by the simple theoretical model for sputtering.

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1. INTRODUCTION

Gold-palladium alloy surfaces have been used as catalysts in numerous investigations. Those studies are summarized in several review papers [1-3]. The proper interpretation of the catalytic studies requires knowledge of the surface composition of the alloy. Several experimental studies have been published in the last few years indicating that the surface composition of the metal binary alloys is different from the bulk composition ([4] and references contained therein). This difference was explained as due to different free energies of components in the surface and bulk phases (regular solution theory) [5-7], or as due to different sizes of atoms constituting an alloy that introduces strain in the crystal lattice [8]. As a result, the surface is enriched in the constituent that minimizes the total free energy of the system or minimizes the lattice strain energy.

The surface composition of the gold-palladium system was recently studied by Auger electron spectroscopy (AES) [9]. The alloy samples under investi-

gation were in the form of microspheres (approximately 50 μm in diameter), and in the form of smaller alloy particles supported on alumina. The $\text{N}_7\text{O}_{4,5}\text{O}_{4,5}$ gold Auger transition (71 eV), and $\text{M}_5\text{N}_{4,5}\text{N}_{4,5}$ palladium transition (330 eV) were utilized for quantitative surface analysis. This study has found that the surface composition as monitored by AES was identical to the bulk composition within the accuracy of the experiments. We have carried out AES studies of the surface composition of the gold-palladium system using bulk polycrystalline samples with flat, polished surfaces. After careful cleaning and equilibration of the samples, significant gold enrichment of the surface was found, especially in the palladium-rich region. Our results deviate considerably from the surface composition predicted for this system by the regular solution theory.

2. EXPERIMENTAL

All Auger electron emission measurements were made with a Physical Electronics (PHI Model 10-150) single pass cylindrical mirror analyzer. The samples were bombarded with 4 keV, 15 μA electron beam. A 5500 Hz modulation frequency with a 2 Vp-p amplitude was used. The surfaces were cleaned by sputtering with 1.5 keV Ar^+ ions generated by a Physical Electronics (PHI, Model 04-161) ion gun. The Ar^+ beam was at the angle 20° to the surface plane and gave a collected current of about 20 μA . The sputtering was taking place in the vicinity of CMA. To avoid changes in the CMA characteristics by deposition of sputtered material in the analyzer [10], a special shutter was constructed closing the orifice of the CMA during extensive sputtering of the samples.

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The samples were prepared by melting together weighed amounts of 5 N palladium and 6 N gold. The bulk atom fractions of palladium, x_b^{Pd} , were then calculated from the weights of pure metals before alloying. The resulting buttons were cold rolled to the thickness 0.30-0.35 mm, and strips were cut to the size 5x25 mm. The samples were abraded by means of emery paper starting with 0 grit (~20 μm) down to 0000 grit (~10 μm). This was followed by polishing with the 1 μm diamond paste in the case of palladium and palladium-rich alloys or with the 6 μm diamond paste in the case of gold and gold-rich samples. The polishing was finished with water suspended 0.05 alumina. This process was continued until the surface was free of scratches as seen with an optical microscope. Then the samples were mounted in the tantalum frame in such a way that they could be heated resistively up to 700°C. They were positioned in the chamber by means of a high precision manipulator (Huntington MM-100). The distances from the samples to the CMA were determined in the usual manner, i.e., by maximizing the height of the peak corresponding to elastically reflected electrons (2000 eV) [11]. The temperature of the samples was monitored by means of Pt and Pt 10% Rh thermocouples or with an infra-red pyrometer. For quantitative analysis of the surface composition the same Auger electron transitions were used as in the study by Wood and Wise [9], i.e., the 71 eV gold transition and 330 eV palladium transition. In addition, we have taken into account the high energy $M_{5/2}N_{7/2}$ gold transition (2024 eV) to establish more conclusively the differences between the surface and bulk compositions. The approximate thickness of the surface layer sampled by Auger electrons (escape depth) is equal to 4 Å for 70 eV Au transition, 30 Å for 2024 eV Au transition, and 8 Å for 330 eV Pd transition. The escape depths are basically the same

as those chosen for AuAg [11] and AuCu [12] alloys, by application of the universal curve [13].

Wood and Wise cleaned the AuPd samples by heating to 450°C for 15 min in a stream of oxygen [9]. In the present work more elaborate procedure was applied. The samples were repeatedly sputtered and then annealed in order to remove impurities from the surface. Sulphur and phosphorus were the main contaminants in the case of palladium and palladium-rich samples. They are likely to originate from the bulk of the alloy. Those contaminants were removed most effectively by sputtering and simultaneous heating at ~600°C. Chlorine as well as traces of argon after sputtering were removed just by annealing. On gold and gold-rich samples there were traces of carbon and oxygen which were easily removed by sputtering at room temperature. The cleaning procedure was continued until the Auger peaks corresponding to contaminants diminished to the background level or completely disappeared. Figure 1 demonstrates the cleanliness of surfaces of pure metals and of the 90.1% Pd alloy so prepared. The spectra from the pure metals agree well with spectra previously published [14].

3. RESULTS

3.1 Equilibration of surface and bulk compositions.

The kinetics of the surface equilibration with the bulk was studied for each sample. After extensive sputtering at the argon pressure 5×10^{-5} Torr (1000-3000 sec) the ratio of Auger electron intensities, $I_{71}^{\text{Au}}/I_{330}^{\text{Pd}} \equiv R(71/330)$, was measured as a function of time in the temperature range 300-670°C. It was found that the surface can be fully equilibrated with the bulk above 500°C (Fig. 2). In the temperature range 500-670°C the ratio $R(71/330)$ after equilibration was found to be practically independent of temperature. Based on these experiments, the temperature 600°C was chosen for equilibration

of the surface of all of the AuPd alloys. As follows from Fig. 2, the surface equilibrates at this temperature in about 500 sec. The samples studied in this work were annealed at 600°C for at least 1000 sec before measurements to ensure complete equilibration. The samples were then quenched to room temperature. It was found recently that quenching increases the surface concentration of the segregating metal [15] when the sample is quenched over a broad temperature range. In that study, the peak ratio measured for a AuNi alloy at annealing temperatures above 700°C differed from the same peak ratio measured after quenching, whereas measurements below 700°C agreed with measurements on the quenched sample. In the case of the AuPd alloy we can expect that the disturbance of the surface composition caused by quenching should not be significant, because we found the temperature dependence of the peak ratio $R(71/330)$ negligible. Also, the sample quenches very fast through a relatively narrow temperature range; the temperature drops from 600°C to 400°C in 25 sec. Below 400°C the surface segregation is a very slow process.

3.2 Auger electron intensity ratios.

After extensive sputtering of the clean samples the peak heights were recorded at several different areas on the surface. At each point the 71 eV and 2024 eV gold peaks, and 330 eV palladium peak were recorded twice. This recording was made as fast as possible (~100 sec) to avoid the drift in intensity of the electron beam. Also, at each point the presence of impurities was checked. The samples were then equilibrated at 600°C and the recording of peak heights was carried out in the same way as previously. The process of sputtering and annealing the samples followed by measurements

in several areas of the alloy surface was repeated until reproducible results were obtained.

A slight distortion was observed in the 71 eV gold peak in the palladium-rich alloys, due probably to the coincidence with a small broad palladium peak. Since the gold peak is much narrower, the proportionality of its height to the Auger electron intensity is probably not significantly affected, and no correction was applied.

The peak ratios $R(71/330)$, $R(2024/330)$, and $R(71/2024)$ were calculated as arithmetic averages from at least 27 values in the case of equilibrated surfaces, and as averages from 18 values in the case of surfaces after sputtering. For every value of the ratio $R(E/E')$ the 0.95 confidence limits were calculated using the formula: $R(E/E') = \bar{x} \pm t_{k-1}s/\sqrt{k}$. Here $\bar{x}$ is the arithmetic average of observed values $R(E/E')$, k is the number of measurements, s is the estimated standard deviation. The number t_{k-1} is chosen so that the probability of the relation $|t| < t_{k-1}$ is equal to 0.95, where t is the Student random variable with $k-1$ degrees of freedom. The results, i.e., the peak ratios $R(71/331)$, $R(2024/331)$, $R(71/2024)$, and the corresponding confidence limits for both equilibrated and sputtered samples are listed in Table 1. Those results are normalized by dividing them by the appropriate intensity ratios, $R^0(E/E')$, measured for the pure metals. Let us denote the normalized peak ratio by $N(E/E') = R(E,E')/R^0(E,E')$. The peak ratios after normalization, i.e., $N(71/330)$, $N(2024/330)$ and $N(71/2024)$, are shown in Figs. 3-5. In the case of 99% Pd alloy, the 2024 eV gold peak was too weak to be recorded. Moreover, after sputtering this sample, the 71 eV gold peak almost disappeared. Therefore for this alloy only the $R(71/330)$ ratio after equilibration is listed. The diagonal

lines in Figs. 3 and 4 correspond approximately to the situation when there is no surface segregation. It is apparent from Fig. 3 that the surfaces of the equilibrated alloys are enriched with gold, and the difference in concentration between the bulk and surface phases increases with increasing bulk Pd content. As it was mentioned earlier, the escape depth of electrons with energy 2024 eV is about 30 Å whereas the escape depth of 71 eV electrons is 4 Å. Thus, the lower energy electrons are much more surface sensitive. This is the cause of the difference between the ratios $N(71/330)$ and $N(2024/330)$, the former deviating from the diagonal line more strongly. Figure 5 shows the dependence of the normalized ratio of both gold peaks for the equilibrated samples, $N(71/2024)$, on the bulk composition. The greater than unity value of this ratio is further proof of the gold segregation to the surface.

After extensive sputtering the surface seems to be slightly enriched with palladium (Fig. 4).

4. DISCUSSION

4.1 Conversion of normalized Auger electron intensity ratios to surface atom fractions.

The approximate formula relating the current I_E , due to the Auger electrons having energy E , with the concentration of component A in the surface region has the following form [11]

$$I_E = k_E r_E c \sum_{n=1}^{\infty} x_n^A \exp(-z_n/\lambda_E \cos\theta), \quad (1)$$

where k_E is a constant depending upon properties of the solid and upon instrumental parameters, r_E is the backscattering factor, c is the number of atoms per unit surface area, x_n^A is the concentration of component A in the n -th layer, z_n is the distance of the n -th layer from the surface, λ_E

is the escape depth of electrons and θ is the acceptance angle of analyzer.

Let us assume that k_E and r_E are independent of composition of the alloy.

It has been found that the escape depths of electrons are functions of energy, but change only slightly from one transition metal to another [13].

It is then reasonable to assume that they do not depend on the alloy composition. The quantities c and z_n are functions of the alloy lattice constant,

$a^{(\text{alloy})}$. For the (111) fcc surface we have $z_n = n a^{(\text{alloy})}/\sqrt{3}$. Since

Vegard's law is valid in the case of most binary alloys forming continuous

series of solid solutions we can assume that $a^{(\text{alloy})} = a^B + (a^A - a^B)x_B^A$,

where a^B and a^A are the lattice constants of pure metals. The quantity

c is proportional to $1/[a^{(\text{alloy})}]^2$.

Let us denote by ξ_E the ratio of intensity of Auger electrons from an alloy, $I_E^{(\text{alloy})}$, to that from the pure metal, I_E^0 . Taking into account

(1) we have [12]

$$\xi_E = \frac{\sum_{n=1}^{\infty} x_n^A \exp(-z_n^{(\text{alloy})}/\lambda_E \cos \theta)}{f \sum_{n=1}^{\infty} \exp(-z_n^A/\lambda_E \cos \theta)}, \quad (2)$$

where $f = [a^{(\text{alloy})}/a^A]^2$. The quantities measured experimentally are the

normalized peak ratios defined by

$$N(E/E') = \frac{R(E/E')}{R^0(E/E')} = \left(\frac{I_E}{I_{E'}} \right) / \left(\frac{I_E^0}{I_{E'}^0} \right) = \xi_E / \xi_{E'}. \quad (3)$$

After substitution of Eq.(2) into Eq.(3), we can express the normalized peak

ratio, $N(E/E')$, in terms of concentrations x_n , lattice constants, and

escape depths. Let us assume that the surface segregation does not extend

beyond the first layer, i.e., let the second, third and all deeper layers

have the same composition as the bulk of the alloy. The surface composition

of AuPd alloys was calculated by three methods having various degrees of

accuracy. The first method is the least accurate because it neglects the attenuation of the Auger electrons. The other two methods take attenuation into account; the second method is based on only one normalized intensity ratio, whereas the third method is based on all of the Auger peak intensity ratios. For this reason the third method gives probably the most reliable results.

First method

It is assumed that all the Auger electrons are produced only in the first layer, and that $a^A \approx a^B$. Then, we have, from Eq.(2): $\xi_E = x_1 = x_S$. If energy E corresponds to Auger electrons from gold, and E' to Auger electrons from palladium we obtain

$$N(E/E') = x_S^{Au} / x_S^{Pd}$$

or

$$x_S^{Pd} = 1/[1 + N(E/E')].$$

The lowest Auger electron energies, i.e., the 71 eV gold transition and the 330 eV palladium transition, should be chosen using this method to compute the surface composition because the escape depths of electrons ought to be as small as possible.

Second method

As follows from Eqs.(2) and (3), $N(E/E')$ is a function of composition of the first layer, x_1^A , the bulk composition, x_b^A , lattice constants and escape depths. The surface composition of the first layer can be calculated from the equation

$$N(\text{exp}) = N(x_1^A),$$

where $N(\text{exp})$ is the experimentally measured normalized ratio, and $N(x_1^A)$ is the function given by formulas (2) and (3). The root of this equation,

$x_1^A = x_S^A$, is the surface concentration of palladium. The calculations

in this paper were performed for the same energies as in the case of the first method, i.e., 71 eV Au and 330 eV Pd.

Third method

The surface composition is assumed to be equal to a value of x_1^{Pd} such that the function F defined below has the minimum value

$$F(x_1^{\text{Pd}}) = \sum_i [N^i(\text{exp}) - N^i(x_1^{\text{Pd}})]^2,$$

where summation extends over all normalized peak ratios, i.e., $N(71/330)$, $N(2024/330)$, and $N(71/2024)$. In other words, a value of $x_1^{\text{Pd}} = x_s^{\text{Pd}}$ is

chosen so that the deviations between experimental and calculated values of normalized peak ratios have the minimum value.

The results of these calculations, i.e., the surface compositions calculated by all three methods, are presented in Table 2. All methods indicate surface enrichment with gold after equilibration at 600°C, and palladium enrichment after sputtering. The differences between surface compositions after equilibration and sputtering are shown in Fig. 6.

4.2 Comparison of experimental results with theoretical predictions.

The regular solution theory has proven to be very useful in predicting the surface composition of binary metal alloys [5,7,29]. The parameters used in calculations are based on the thermodynamic data available for an alloy: heats of sublimation of pure metals, $\Delta H_{\text{sub}}^{\text{Pd}}$, $\Delta H_{\text{sub}}^{\text{Au}}$, heats of mixing ΔH_m or activity coefficients. In the case of monolayer model the surface composition x_s^{Pd} is the root of the equation [5-7].

$$RT \ln \frac{x_s^{\text{Pd}}(1-x_b^{\text{Pd}})}{x_b^{\text{Pd}}(1-x_s^{\text{Pd}})} + 2\Omega N_o Z[(\ell+m)x_b^{\text{Pd}} - \ell x_s^{\text{Pd}} - m/2] + m(\Delta H_{\text{sub}}^{\text{Pd}} - \Delta H_{\text{sub}}^{\text{Au}}) = 0, \quad (4)$$

where R is the gas constant, N_0 is Avogadro's number, Z is the total number of first nearest neighbors, ℓ is the fraction of first nearest neighbors in the same plane, m is the fraction of first nearest neighbors in the adjacent plane. For the (111) fcc plane $\ell = 0.5$, $m = 0.25$, $Z = 12$. Ω is the regular solution parameter expressed in terms of bond energies

E_{ij} : $\Omega = E_{PdAu} - \frac{1}{2}(E_{PdPd} + E_{AuAu})$. This parameter can be calculated from

the relation [11]: $\Omega N_0 = \Delta H_m / Z x_b^{Au} x_b^{Pd}$. In the tables of thermodynamic functions we find: $\Delta H_{sub}^{Pd} = 90\,000$ cal/mole, $\Delta H_{sub}^{Au} = 88\,000$ cal/mole [16].

The average value of ΩN_0 calculated from heats of mixing at 298 K [17] is equal to -620 cal/mole. The calculated surface composition for the AuPd alloy is compared in Fig. 7 with experimental results obtained in the present work and those obtained by Wood and Wise [9]. The theory predicts insignificant surface enrichment with gold or palladium, and agrees with their experimental results. The surface composition obtained in the present work deviates considerably from the regular solution theory prediction, especially in the case of palladium-rich samples. The observed gold enrichment cannot be justified by the strain theory, as the difference in sizes of gold and palladium atoms is rather small (less than 5%).

The difference between our results and those by Wood and Wise can be rationalized in several ways. In their calculations of the surface composition, Wood and Wise did not take into account the attenuation of Auger electrons using our first method of data analysis. As it follows from inspection of Table 2 and Fig. 7, the surface enrichment with gold that is obtained from the first method of calculations is much less pronounced than that resulting from the other two methods taking into account electron attenuation. In the case of smaller number of measurements for a given

alloy sample this enrichment may not be easily noticeable. The other cause of discrepancy can be a different sample geometry. We have used alloy samples with the flat, polished surfaces as compared to microspheres in their studies. It should be noted that the absence of surface roughness is tacitly assumed in all methods of calculations of the surface composition.

Maire et al. recently published their studies on surface segregation in the AuPd alloy containing 22 at.% Pd [18]. The AES analysis was based on the 71 eV gold and 330 eV palladium Auger transitions. The authors cleaned the sample in the same way that we employed in our work, i.e. by sputtering and annealing cycles. The surface concentration of palladium, calculated without taking into account the attenuation of Auger electrons, was equal to 17.7%. The gold surface enrichment found by Maire et al. is consistent with our observations on gold-rich alloy samples (Fig. 7).

4.3 The effect of sputtering on the surface composition.

Shimizu et al. [19] introduced a simple model predicting the surface composition of binary metal alloys, AB, after extensive sputtering. The surface concentration, x_s^A , was expressed in terms of sputtering yields, S_A and S_B , defined as the average number of atoms ejected from the target per incident ion Ar^+ . The authors assumed that the relative sputtering yield S_B/S_A in the case of alloy is the same as the ratio of sputtering yields of pure metals. The resulting expression has the following form [19]

$$x_s^A = R_o x_b^A / (1 - x_b^A + R_o x_b^A) \quad (5)$$

where $R_o = S_B/S_A$. This formula was proven to be valid for the CuNi[19], AgPd[20], and NiPd[20] alloys. The published values of the sputtering yields for pure Au and Pd were measured up to energy 600 eV [21,22]. They are shown in Table 3. Using the ratio S_{Au}/S_{Pd} for 600 eV in the calculations

instead of 1500 eV, probably underestimates the palladium enrichment, because this ratio is growing with increasing energy of Ar^+ ions. In fact, the experimentally determined palladium enrichment is stronger than that predicted by formula (5) (Fig. 8).

4.4 The effect of electron backscattering.

In the estimation of the surface composition of AuPd alloy we assumed that the backscattering factor r_E is the same for pure metals as for the alloys. In reality this is not always the case. It has been found that the backscattering factor increases with the atomic number and the incident beam energy [23,24]. Let us assume at present that the backscattering factor in AuPd alloys increases with increasing gold content from pure palladium to pure gold. Then the current of backscattered electrons from an alloy is smaller than that from pure gold and the following inequality holds

$$\xi_{\text{Au}}^{\text{observed}} = I_{\text{Au}}^{(\text{alloy})} / I_{\text{Au}}^{\text{true}} < \xi_{\text{Au}}^{\text{true}},$$

where the true value of the ratio ξ corresponds to a situation with no backscattering or to a situation with $r_E = \text{const}$. Conversely,

$$\xi_{\text{Pd}}^{\text{observed}} > \xi_{\text{Pd}}^{\text{true}}.$$

In the case of gold-to-palladium normalized peak ratios we have

$$N^{\text{true}} = \xi_{\text{Au}}^{\text{true}} / \xi_{\text{Pd}}^{\text{true}} > N^{\text{observed}},$$

$$x_{\text{S}}^{\text{Pd}}(\text{true}) = 1 / (1 + N^{\text{true}}) < 1 / (1 + N^{\text{observed}}) = x_{\text{S}}^{\text{Pd}}(\text{observed}).$$

Thus, it follows from the first method of calculation of the surface composition that the true gold concentration in the surface region is probably even higher than that calculated from experimental data. Also, the observed discrepancy between observed and theoretically predicted values of surface composition after sputtering can be partially due to backscattering.

4.5 The effect of ordering in the AuPd alloy.

The regular solution parameter, Ω , for the AuPd alloy has a large negative value, therefore a strong tendency towards ordering should be expected. In fact, there is experimental evidence indicating short range order in this alloy [25]. There is also evidence of long range order, but this was found only in the case of evaporated AuPd films [26-28]. No long range order has been found in the bulk alloys [28]. Equation (4) describing the surface composition was derived assuming complete disorder in the alloy. It has been shown [29] that taking into account the short range order in the regular solution theory does not produce significant changes in surface composition, so that the discrepancy between regular solution theory and experiment in the present work is not due to ordering in the AuPd alloy.

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FIGURE CAPTIONS

- Fig. 1. The spectra of clean surfaces; pure metals and the 90.1% Pd alloy.
- Fig. 2. The kinetics of surface equilibration. The $R(71/330)$ peak ratio is shown as a function of annealing time after sputtering:
 ∇ -300°C, $\square$ -400°C, Δ -500°C, $\circ$ -600°C.
- Fig. 3. The $N(71/330)$ and $N(2024/330)$ normalized intensity ratios after equilibration at 600°C versus the ratio of bulk atom fractions, x_b^{Au}/x_b^{Pd} .
- Fig. 4. The $N(71/330)$ and $N(2024/330)$ normalized intensity ratios after sputtering versus the ratio of bulk atom fractions, x_b^{Au}/x_b^{Pd} .
- Fig. 5. The normalized intensity ratio of two gold peaks, $R(71/2024)/R^0(71/2024)$, as a function of bulk composition.
- Fig. 6. The surface atom fraction, x_s^{Pd} , as a function of bulk atom fraction, x_b^{Pd} ; Δ -after sputtering, $\circ$ -after equilibration in 600°C. Third method of calculations (explained in the text).
- Fig. 7. The surface atom fraction, x_s^{Pd} , as a function of bulk atom fraction, x_b^{Pd} for equilibrated alloys. Δ -results of Wood and Wise for microspheres [9]; $\square$ -Maire *et al.* [18]; ∇ -this work, first method of calculations; $\circ$ -this work, third method of calculations. The solid line corresponds to the regular solution theory prediction.
- Fig. 8. The surface atom fraction, x_s^{Pd} , as a function of bulk atom fraction, x_b^{Pd} , after sputtering; third method of calculations. The solid line corresponds to theory prediction [Eq.(5)].

Table 1. The R(71/330), R(2024/330) and R(71/2024) peak ratios with 0.95 confidence limits.

x_b^{Pd}	(a) after equilibration in 600°C		
	R(71/330)	R(2024/330)	R(71/2024)
0.0103	67.3±1.5	4.44±0.11	15.2±0.2
0.1035	7.42±0.08	0.457±0.007	16.3±0.2
0.4024	1.28±0.01	0.0693±0.0008	18.4±0.2
0.6949	0.499±0.009	0.0172±0.0004	28.9±0.4
0.9010	0.247±0.006	0.00507±0.00017	48.6±0.8
0.9901	0.0400±0.0010		
pure metals	0.549±0.006	0.0340±0.0009	16.1±0.2

x_b^{Pd}	(b) after sputtering		
	R(71/330)	R(2024/330)	R(71/2024)
0.0103	30.0±0.9	1.94±0.05	15.5±0.2
0.1035	3.48±0.04	0.238±0.004	14.7±0.1
0.4024	0.788±0.005	0.527±0.0005	14.9±0.2
0.6949	0.186±0.010	0.0112±0.0008	16.7±0.5
0.9010	0.0487±0.0038	0.00269±0.00023	18.2±0.7
pure metals	0.561±0.011	0.0351±0.0015	16.0±0.5

Table 2. Surface compositions of the AuPd alloys calculated from normalized peak ratios by means of three methods (explained in the text)

(a) after equilibration at 600°C

x_b^{Pd}	x_s^{Pd}		
	Method 1	Method 2	Method 3
0.0103	0.0081±0.0002	0.0075±0.0007	0.0067±0.0009
0.1035	0.0690±0.0010	0.0333±0.0032	0.0304±0.0049
0.4024	0.300±0.003	0.229±0.008	0.231±0.013
0.6949	0.524±0.005	0.396±0.012	0.312±0.017
0.9010	0.690±0.006	0.524±0.011	0.257±0.023
0.9901	0.932±0.002	0.896±0.003	

(b) after sputtering

x_b^{Pd}	x_s^{Pd}		
	Method 1	Method 2	Method 3
0.0103	0.0183±0.0007	0.0434±0.0023	0.0429±0.0027
0.1035	0.139±0.003	0.255±0.008	0.253±0.013
0.4024	0.417±0.005	0.527±0.012	0.531±0.021
0.6949	0.751±0.010	0.868±0.018	0.758±0.023
0.9010	0.920±0.006	0.959±0.010	0.876±0.012

Table 3. Sputtering yields for gold and palladium under Ar^+ ion bombardment [21,22]

E (keV)	S_{Au}	S_{Pd}
0.1	0.3	0.4
0.2	1.1	1.0
0.3	1.6	1.4
0.5	2.4	
0.6	2.8	2.4

XBL7611-7001

Fig. 1

Fig. 2

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Fig. 3

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Fig. 4

Fig. 5

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Fig. 6

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Fig. 7

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Fig. 8

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