



## Direct Observation of the Surface Segregation of Cu in Pd by Time-Resolved Positron-Annihilation-Induced Auger Electron Spectroscopy

J. Mayer,<sup>1,2,\*</sup> C. Hugenschmidt,<sup>1,2</sup> and K. Schreckenbach<sup>1,2</sup>

<sup>1</sup>ZWE FRM II, Lichtenbergstraße 1, 85747 Garching, Germany

<sup>2</sup>Physik Department E21, Technische Universität München, James Franck Straße, 85748 Garching, Germany<sup>†</sup>

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Density functional theory calculations predict the surface segregation of Cu in the second atomic layer of Pd which has not been unambiguously confirmed by experiment so far. We report measurements on Pd surfaces covered with three and six monolayers of Cu using element selective positron-annihilation-induced Auger electron spectroscopy (PAES) which is sensitive to the topmost atomic layer. Moreover, time-resolved PAES, which was applied for the first time, enables the investigation of the dynamics of surface atoms and hence the observation of the segregation process. The time constant for segregation was experimentally determined to  $\tau = 1.38(0.21)$  h, and the final segregated configuration was found to be consistent with calculations. Time-dependent PAES is demonstrated to be a novel element selective technique applicable for the investigation of, e.g., heterogeneous catalysis, corrosion, or surface alloying.

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Pure Pd and Pd-based alloys are important materials, e.g., for hydrogen storage, hydrogen purification, and heterogeneous catalysis. In particular, in Cu-Pd alloys the amount of Cu atoms and their exact position strongly affect the mechanical stability and the catalytic properties of Pd membranes [1–3]. Density functional theory calculations for Cu-Pd alloys predict the segregation of Cu in the second atomic layer of Pd [4,5], but the available experimental data for this system are still poor and the experiments done so far do not unambiguously confirm the theory [6–8].

In the presented experiment we investigate the stability and dynamics of thin Cu layers on the surface of polycrystalline Pd. In our approach, we use the extremely surface sensitive and elemental selective analysis method of positron-annihilation-induced Auger electron spectroscopy (PAES) for the direct measurement of the surface segregation. In contrast to electron-induced Auger electron spectroscopy (EAES), which was applied as well, PAES intrinsically analyzes the topmost atomic layer of a sample almost exclusively [9–11]. In addition to the high surface sensitivity that arises from the efficient trapping of the positrons in a delocalized surface state, one benefits from the positron affinity  $A^+$  which makes PAES a highly elemental selective technique [12]. Consequently, if more than one element is present at the surface, the positrons are attracted to the atoms with a higher relative positron affinity and thus annihilate preferably with electrons of the respective element [13].

Until now, the time for a single PAES measurement amounted to several days, and hence it was not possible to investigate dynamic surface processes. We cope with this challenge by using the high intensity neutron-induced positron source Munich (NEPOMUC) which delivers  $9 \times 10^8$  monoenergetic positrons per sec-

ond [14]. Additionally, the experimental setup was improved [15,16] in order to enable time dependent PAES and hence to monitor the dynamic behavior of Cu atoms on a Pd surface for the first time.

For the presented PAES experiments a remoderated 20 eV positron beam with an intensity of  $4 \times 10^7 \frac{e^+}{s}$  and a diameter of 5 mm FWHM at the sample site was used [17]. The pressure in the analysis chamber amounted to  $p < 3 \times 10^{-9}$  mbar, and all experiments were carried out at room temperature. The pure samples, polycrystalline Cu (purity > 99.999%) and polycrystalline Pd (purity > 99.95%), with dimensions of  $20 \times 20$  mm were annealed and sputtered with an  $Ar^+$ -ion beam of 1 keV energy. The Pd samples were coated with 2.88 atomic monolayers (ML) of Cu (sample 1) and 5.77 ML of Cu (sample 2), respectively, using an electron beam evaporator with an evaporation rate of 0.02 nm/s and a chamber pressure of  $p < 2 \times 10^{-8}$  mbar. The evaporation rate was controlled with a piezo thickness monitor. In addition to PAES, all samples have also been characterized with EAES as a complementary method.

With the intense low energy positron beam NEPOMUC and an improved setup of the PAES spectrometer [15,16], we succeeded to reduce the measurement time for a single PAES spectrum to seven minutes. This is the shortest PAES spectrum recording time reported so far (compared, e.g., to [18,19]). Figure 1 shows the PAES spectra obtained for clean surfaces of Cu and Pd. The energy resolution amounts to  $\frac{\Delta E}{E} < 5\%$ , and the signal to noise ratio amounts to at least 11:1. The Cu  $M_{2,3}VV$  transition at 60 eV, as well as the Pd  $N_{2,3}VV$  transition at 45 eV and the Pd  $N_1VV$  transition at 80 eV, respectively, are clearly observable (Auger energy reference spectra are from [20]). The different absolute intensities of the respective peaks are due to the different core annihilation probabilities of the

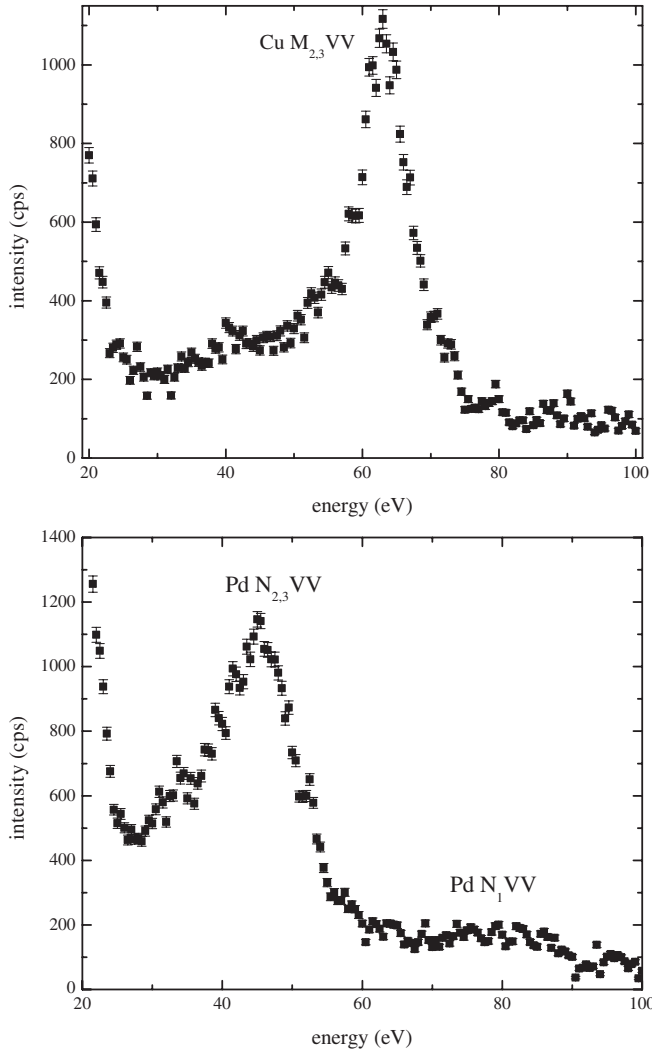


FIG. 1. PAES spectrum of clean, polycrystalline Cu and Pd, respectively. The acquisition time for each spectrum amounts to seven minutes, recorded at the high intensity positron source NEPOMUC in Munich.

primary hole,  $p_{\text{core}}$ . For the Cu  $3p$  level (corresponding to the Cu  $M_{2,3}VV$  transition)  $p_{\text{core}}$  amounts to 5.93%, for the Pd  $4p$  level to 6.07%, and for the Pd  $4s$  level to 1.51% (corresponding to the Pd  $N_{2,3}VV$  transition and the Pd  $N_1VV$  transition, respectively) [11]. Since the primary holes in the Pd  $4s$  level contribute also to the Pd  $N_{2,3}VV$  transition, the ratio of the intensities of the two Pd peaks is not identical to the ratio of the respective core annihilation probabilities.

In both cases the intensity between the energy of the impinging positrons ( $E_0 = 20$  eV) and the Auger transition does not drop to zero, because the produced Auger electrons are emitted isotropically from the first atomic layer; thus, inelastically backscattered Auger electrons are detected as well. The background, in particular, at energies higher than the Auger peak, arises from photoelectrons and

Compton electrons, produced by the released annihilation radiation in the sample.

In order to investigate the segregation process at the surface, two Pd samples with different Cu layer thicknesses  $d$  ( $d_1 = 2.88$  ML and  $d_2 = 5.77$  ML) have been measured for 9.2 h and 8.4 h, respectively. The acquisition time amounted to 15 min for each spectrum. The obtained PAES spectra  $I_{\text{Cu/Pd}}(E, t)$ , where  $E$  is the energy in eV and  $t$  is the time in hours, were evaluated as follows: Using linear combinations of the pure reference spectra  $I_{\text{Cu}}(E)$  and  $I_{\text{Pd}}(E)$  (see Fig. 1), the entire spectrum  $I_{\text{Cu/Pd}}(E, t)$  was fitted with the two fitting parameters  $a(t)$  and  $b(t)$ :

$$I_{\text{Cu/Pd}}(E, t) = a(t)I_{\text{Cu}}(E) + b(t)I_{\text{Pd}}(E). \quad (1)$$

Then the fractions of all detected Auger electrons, which stem from Pd [ $F_{\text{Pd}}(t)$ ] and Cu [ $F_{\text{Cu}}(t)$ ], respectively, were determined according to Eq. (2). Since  $F_{\text{Cu}}(t)$  and  $F_{\text{Pd}}(t)$  are relative parameters, any dependency on a possible change in the intensity of the primary beam is eliminated.

$$F_{\text{Cu}}(t) = \frac{a(t)}{a(t) + b(t)} \quad \text{and} \quad F_{\text{Pd}}(t) = 1 - F_{\text{Cu}}(t). \quad (2)$$

In contrast to other data evaluations (e.g., [21]), which use only the range of the Auger peak energy, in the present data analysis the whole spectrum is used for the fitting routine since the shape of the spectrum is altered by varying the layer thickness over the entire energy range. For instance, the reflectivity of the sample increases with increasing atomic number  $Z$  and thus leads to a different shape in the low energy region.

The results of this fitting procedure, i.e., the respective Auger fractions for the two different Cu-Pd samples independent of time, are plotted in Fig. 2.

In the case of 2.88 ML Cu on Pd, the Auger fraction from Cu stays constant for almost 2 h at 87% before it drops within 2 h to a constant value of 70%. Simultaneously, the Pd intensity increases from 13% to 30%. This principal behavior could be reproduced on the sample with 5.77 ML of Cu on Pd: No Pd is observable at all at the beginning; i.e., 100% of the detected Auger electrons emerge from Cu. After about 3 h, Auger electrons emitted from Pd become visible, and the corresponding Auger fraction starts to saturate after an additional 2 h at a value of 14%. The Cu signal stabilizes accordingly at 86% of all detected Auger electrons.

The observed time dependency of the intensities is very well described by an exponential fit of the type

$$F_{\text{Cu}}(t) = Ae^{-(t-t_0)/\tau} + F_{\text{Cu},\infty} \equiv 1 - F_{\text{Pd}}(t) \quad \text{for } t \geq t_0.$$

The fits are plotted for both layers as solid lines in Fig. 2. The starting point  $t_0$  was found by a variation in  $t$ . For sample 1, with 2.88 ML Cu initially, and sample 2, with 5.77 ML Cu on Pd,  $t_0$  reads 1.5 h and 3 h, respectively. The resulting time constants for both samples amount to

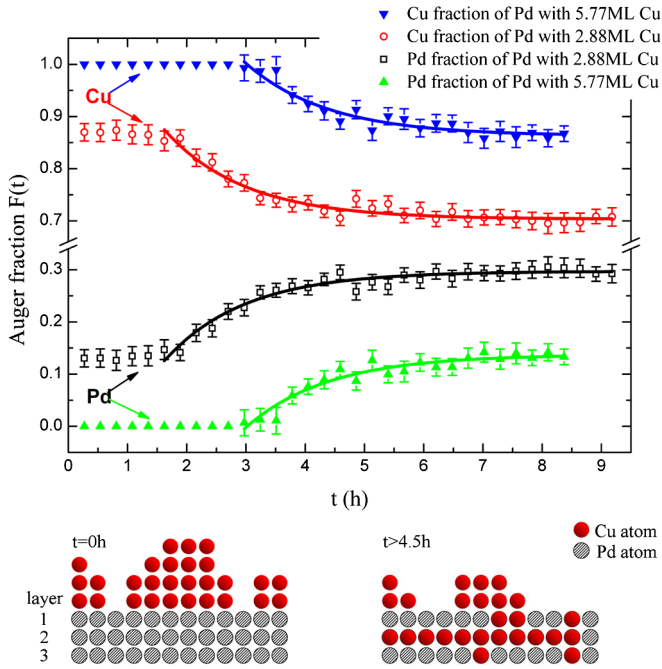


FIG. 2 (color online). Fraction of the Auger intensities from Cu and Pd, respectively, as a function of time for two different Cu covers on Pd: 2.88 ML Cu on Pd and 5.77 ML Cu on Pd. In both cases a similar time dependency is observed due to the segregation of Cu in the second atomic layer of Pd. The solid line is an exponential fit, revealing a time constant of  $\tau \approx 1.38$  h for the creation of the stable Cu layer in the second atomic layer of Pd. At the bottom, the schematic distribution of the Cu atoms on Pd (2.88 ML Cu on Pd) is shown before and after the segregation.

$$\tau_1 = (1.35 \pm 0.20) \text{ h} \quad \text{and} \quad \tau_2 = (1.40 \pm 0.37) \text{ h}$$

and hence agree within the experimental uncertainty. From these values a mean time constant, which characterizes the segregation time of the process, of  $\tau = (1.38 \pm 0.21)$  h is obtained. The according saturation values  $F_{\text{Cu},\infty}$ , where a change in the intensity was no longer observed, are calculated to

$$F_{\text{Cu}1,\infty} = 0.703 \pm 0.005 \quad \text{and} \quad F_{\text{Cu}2,\infty} = 0.863 \pm 0.009.$$

In contrast to PAES, EAES measurements, which have been performed at the beginning and after 8.5 h, did not show any change in the intensities. This is attributed to the reduced surface sensitivity of EAES, since the information obtained with EAES is averaged over several monolayers.

At the sample with an initial Cu coverage of 2.88 ML, a pure Cu signal is not detected, as expected due to the high surface sensitivity of PAES. The observed fraction of 87% Cu Auger electrons at the beginning is first explained by the nonhomogeneous growth of the Cu layer in an island structure [7]. Hence, there is still Pd in the first atomic layer, which is detected by PAES. Second, the difference of the positron affinities of Pd ( $A_{\text{Pd}}^+ = -6.40$  eV [22]) and Cu ( $A_{\text{Cu}}^+ = -4.57$  eV [23]) favors the annihilation of the positrons with electrons from Pd atoms. Thus, if there is

Pd within the diffusion length of the positron at the surface, the positron will annihilate with electrons from Pd atoms rather than from Cu atoms, leading to an enhanced sensitivity for Pd.

In the case of sample 2, with 5.77 ML Cu on Pd initially, no Pd at all is observable at the beginning. Consequently, the entire Pd substrate must be covered with at least one ML of Cu, regarding the relative positron affinities [16].

The exponential intensity profile for both Cu-covered Pd samples is attributed to the migration of Cu atoms from the surface into the second atomic layer of Pd. Alternative interpretations such as surface contamination [24] are dismissed since an increase of  $F_{\text{Pd}}$  at the expense of  $F_{\text{Cu}}$  is observed. Bulk diffusion is also excluded since it would lead to a vanishing Cu intensity, which is in contrast to the measured saturation values  $F_{\text{Cu}1,\infty}$  and  $F_{\text{Cu}2,\infty}$ . Also, surface diffusion is ruled out because it would require time scales of several minutes [25], which is well below the observed value of 1.38 h.

Hence, the observed increase of the Pd Auger intensities at the expense of the Cu intensities until reaching a saturation value is attributed to the segregation of Cu in Pd. The migration of Cu from the surface to the second atomic layer of Pd is shown schematically at the bottom in Fig. 2, where the example of Pd with 2.88 ML of Cu is shown. The reason for this segregation is that the most stable configuration for Cu is in the second atomic layer of Pd in thermodynamical equilibrium. This is supported by the calculated segregation energy of  $E \approx -6$  kJ/mol  $\approx -63$  meV per Cu atom [5]. In this density functional theory calculation, the energy difference for Cu atoms in the first and second atomic layers of Pd is determined relative to the energy of a Cu atom in the third atomic layer of Pd, which corresponds to a bulklike site. The theoretical considerations, however, do not describe the temporal development, but reveal the second atomic layer to be the energetically most favorable layer for Cu atoms. Similar observations for both Cu/Pd samples lead to the conclusion that the energy gain for the Cu atoms is not dependent on the thickness of the Cu cover layer nor is it dependent on time. Hence, the model with an exponential behavior is justified, and we could determine the time constant  $\tau \approx 1.38$  h for the segregation of Cu in Pd for the first time. However, it is surprising that the decrease of the Cu intensity does not start immediately, but after a certain time  $t_0$ . Consequently, the Cu atoms seem to start to diffuse into the Pd at places where the islands are thick and not where only one monolayer of Cu covers Pd.

In this Letter, we presented PAES spectra of polycrystalline Cu and Pd with the unprecedented short measurement time of only seven minutes. Thus, it was possible to observe directly the segregation of Cu in the second atomic layer of Pd by time-dependent PAES, and the theoretically predicted result of the stable end configuration was confirmed experimentally. Moreover, the migration process

itself was observed with a characteristic time constant of  $\tau = (1.38 \pm 0.21)$  h. With time-dependent PAES, it is now possible to measure elemental selective dynamic processes such as heterogeneous catalysis, surface alloying, or corrosion processes of numerous systems with unprecedented measurement times and extremely high surface sensitivity.

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\*Jakob.Mayer@frm2.tum.de

†<http://e21.frm2.tum.de/nepomuc.html>

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