Positron Annihilation Induced Auger Electron Spectroscopy Studies of Submonolayer Au on Cu(100): Direct Evidence for Positron Localization at Sites Containing Au Atoms

K. H. Lee,[1] Gimo Yang,[1] A. R. Koymen,[1] K. O. Jensen,[2] and A. H. Weiss[1]
[1]*Department of Physics, University of Texas at Arlington, P.O. Box 19059, Arlington, Texas 76019*
[2]*School of Physics, University of East Anglia, Norwich NR4 7TJ, United Kingdom*

(Received 26 July 1993)

Positron annihilation induced Auger electron spectroscopy (PAES) performed on submonolayer films of Au deposited on Cu(100) provides direct evidence for preferential annihilation with Au atoms. The PAES intensity of Au is anomalously large at low surface concentrations (e.g., the PAES signal from Au deposited at 173 K reaches ~40% of the signal obtained for a complete monolayer at ~0.07 monolayer). We infer from this behavior and comparisons with model calculations that positrons are localized at sites containing many contiguous Au atoms.

PACS numbers: 68.55.−a, 71.60.+z, 78.70.Bj

A number of the newly developed positron spectroscopies of the surface attain top layer specificity by exploiting the fact that positrons implanted at low energies in metals and semiconductors have a high probability of becoming trapped in an image-correlation well just outside the surface [1]. In most models of the positron surface state, the positron is assumed to be localized only in the direction normal to the surface and is considered to be in a delocalized Bloch state in the plane of the surface [2]. However, the question of whether the positron is further localized within the surface plane at the sites of surface inhomogeneities is of crucial importance in the interpretation of angular correlation of annihilation radiation (ACAR) measurements of the local electronic structure of the surface [3], extracting surface concentrations from positron annihilation induced Auger electron spectroscopy (PAES) [1], and in understanding contrast in the positron reemission microscope [1]. In addition, positrons localized within the surface plane could serve as model systems for the study of particles confined such that their quantum mechanical behavior becomes paramount as in the case of electrons confined in quantum corrals [4].

The possibility of localization of the positron at surface vacancies and step edges has been explored theoretically, but no firm conclusions can be drawn from these calculations because they are strongly model dependent [2,5]. Several experimental results have suggested that positrons are not in a delocalized surface state. High resolution measurements of the angular correlation of annihilation radiation from an Al surface [3] did not exhibit an expected anisotropy relative to the surface normal and studies of positron and positronium emission indicated a reduction in emissions following sputter damage or following the growth of a presumably defected overlayer [6]. However, these effects may be alternatively explained without invoking localization in terms of many body effects [7] in the case of the ACAR measurements and in terms of surface induced changes in branching ratios in the positron and Ps emission studies.

Here we present the results of measurements using PAES performed on submonolayer films of Au deposited on annealed and sputtered Cu(100) which give direct evidence for the localization of positrons at sites on the surface occupied by Au adatoms. PAES peak intensities for a given element are proportional to the probability of creating a core hole in atoms of that element which is in turn proportional (within the independent particle model) to the overlap of the positron wave function with the wave functions of the core electrons of that element. Previous studies have demonstrated that the positrons giving rise to the PAES signal are localized (at least in the direction perpendicular to the surface) in the image potential well just outside the surface [8,9] and that consequently PAES is almost exclusively a probe of the topmost atomic layer [10]. Here, we report results which indicate an anomalously large PAES intensity for Au after deposition at 173 K, corresponding to a small fraction of a monolayer [e.g., the PAES signal from Au reaches ~40% of the signal obtained for a complete monolayer (ML) at ~0.07 ML of Au]. We also found that the degree of low coverage enhancement was highly sensitive to sputter damage. Theoretical modeling indicates that our data are not consistent with either a delocalized positron or with a positron bound to single gold atom but can be accounted for by the localization of positrons on Au islands. In addition we observed changes in the PAES intensities as the sample is warmed from 173 to 303 K which provide a direct indication of intermixing and the formation of a surface alloy of Au and Cu in the topmost layer.

The experiments were performed using the UT Arlington PAES system, described previously [11]. Gold was evaporated onto a Cu(100) substrate at 173 K. Data were then taken at 173 K using PAES, electron-induced Auger electron spectroscopy (EAES), and LEED. Subsequently the sample was warmed first to 303 K and later to 423 K without changing the amount of Au deposited and data were obtained at these two temperatures. The amount of gold deposited was determined from the deposition time after a fixed evaporation rate was established using a quartz microbalance. At 303 K, the best $c(2\times2)$ LEED pattern was observed between the Au deposition

0031-9007/94/72(12)/1866(4)$06.00

times of 250 and 300 sec. Based on our LEED results and the observation by Graham that the best $c(2\times2)$ LEED pattern is obtained at 0.5 ML [12] we take a time of 550 ± 50 sec as corresponding to 1 ML deposition. This calibration is consistent with an estimate of 440 $\pm$ 100 sec/ML determined from the quartz microbalance. At 173 K, a $P(1\times1)$ LEED pattern was observed for the clean Cu(100) and this pattern then became diffuse as the Au coverage increased. A $c(2\times2)$ LEED pattern was observed between 0.36 and 0.64 ML of Au deposition at 303 K.

The spectrum shown in the inset of Fig. 1(a) was obtained at 173 K directly after deposition of 0.55 ML of Au. The spectra shown in the inset of Fig. 1(b) was obtained after the sample was heated to 303 K at the same coverage. The primary PAES peaks (Au $O_{23}VV$, Cu $M_{23}VV$) are indicated in the inset. The Auger peaks from other transitions that originate from more tightly bound core levels are predicted to be much smaller than the primary peaks and are not observable in our measurements [13]. Comparing the results shown in Figs. 1(a) and 1(b) for depositions below 1 ML, it can be seen that as the sample is warmed from 173 to 303 K, the Cu PAES intensity increases while the Au intensity decreases, indicating an intermixing of Au and the formation of the surface alloy layer as also indicated by LEED. The ratio of Au $O_{23}VV$ (42 eV) to Cu $M_{23}VV$ (60 eV) PAES intensity for the spectra shown in the insets changed from 3.4 ± 0.8 to 1.5 ± 0.2 upon warming from 173 to 303 K and then to 1.06 ± 0.15 upon further warming to 423 K, while EAES spectra for the same deposition (0.55 ML) show only a small change in the peak to peak amplitudes of the prominent low energy AES peaks. Specifically, the ratios of the Au (69 eV) to Cu (60 eV) AES signal are 0.66 ± 0.03, 0.56 ± 0.03, and 0.45 ± 0.02 at 173, 303, and 423 K, respectively. The large change seen in the PAES spectra is indicative of the enhanced surface selectivity of PAES as compared to EAES which averages over 5–10 atomic layers.

PAES spectra, similar to those shown in the insets of Figs. 1(a) and 1(b), were obtained at 173 and 303 K for 16 different Au depositions ranging from 0 to 1.8 ML. These spectra were then used to obtain PAES intensities for Au and Cu as a function of Au coverage which are plotted in Fig. 1. The Cu and Au intensities were normalized using elemental reference spectra obtained at 173 K from the clean Cu(100) substrate and from the substrate after the deposition of 2 ML of Au. These reference spectra were in good agreement with previous PAES results for high purity Cu and Au foils [13]. Referring to Fig. 1(a) it can be seen that at 173 K the Au PAES intensity increases very rapidly up to ≈ 0.07 ML and then increases more gradually until the Au PAES intensity saturates at about 1 ML while the Cu PAES intensity attenuates to zero. At 303 K, the PAES intensity changes almost linearly up to 0.5 ML and saturates beyond 1.2 ML. Calculated Auger emission probabilities

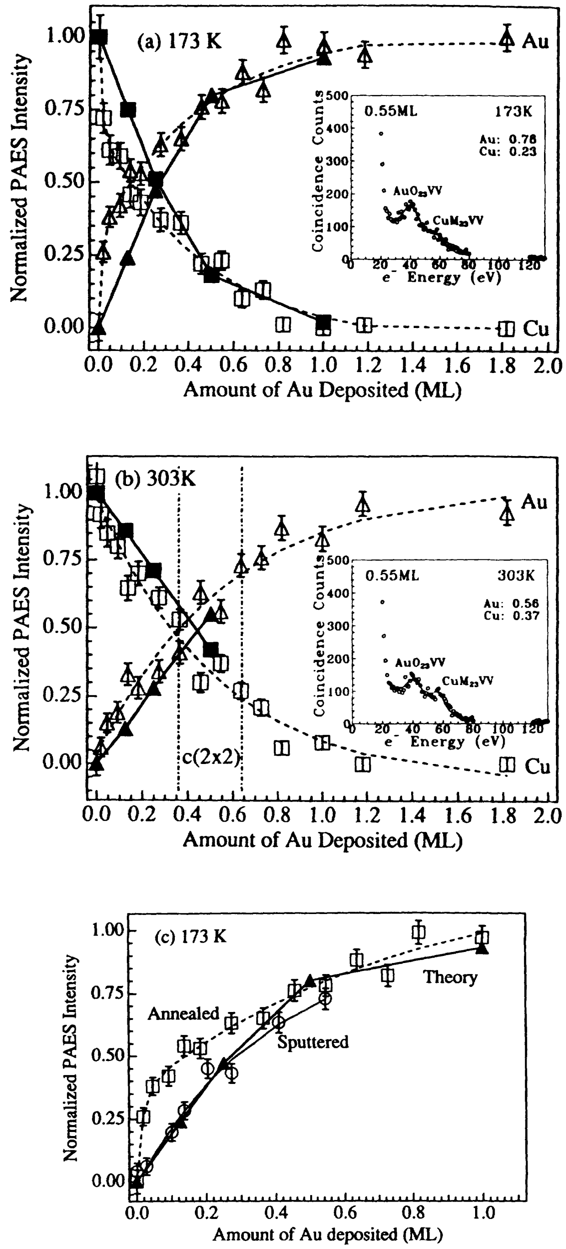

FIG. 1. PAES intensities from a Cu(100) substrate as a function of the amount of Au deposited at 173 K. Intensities from (a) an annealed substrate measured at 173 K and (b) after warming to 303 K. (c) Comparison of measurements on annealed and sputtered substrates. Open triangles (squares) correspond to measured Au (Cu) PAES intensities. Dashed lines are from a fit to a function of the form $A+Be^{cx}$. Solid triangles (squares) (connected by solid lines) represent values of model calculations for the PAES intensities of Au (Cu). The open circles in Fig. 1(c) represent Au PAES intensities obtained from sputtered substrate at 173 K. PAES spectra obtained from a coverage of 0.55 ML Au on Cu(100) at 173 and 303 K are shown in the insets to (a) and (b), respectively. Solid lines in the insets were obtained from a two parameter fit to a linear combination of Au and Cu reference spectra. The normalized PAES intensities determined from the fit are indicated in the upper right of the inset.

for the Au overlayer on the Cu(100) surface and for the Au-Cu alloy are compared with the measured PAES intensities at 173 and 303 K, respectively in Figs. 1(a) and 1(b). The calculations were performed as detailed in Ref. [14] except that the surface dipole term was approximated using the approach of Weinert and Watson [15]. The positron is assumed to be in the ground state of the image correlation well at the surface and is delocalized in the plane of the surface. The potential is modeled using the corrugated mirror model of Nieminen and Puska [2]. The effective potential is constructed on a three dimensional mesh with a spacing between mesh points of the order of 0.1 Å, followed by numerical solution of the ensuing Schrödinger equation. The annihilation characteristics are then calculated from the positron and electron densities. In the calculations performed for comparison with the 173 K data it was assumed that the Au atoms were on top of a complete (100) plane of Cu atoms, while in calculations performed for comparison with the 303 K data it was assumed that the Au atoms replaced Cu atoms in the topmost layer to simulate the alloy surface present at this temperature. In both cases, the calculations were performed for the ordered structures: $c(4\times4)$, $p(2\times2)$, $c(2\times2)$, and $p(1\times1)$ corresponding to depositions of $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$, and 1 ML, respectively. The calculated PAES intensities were taken to be proportional to a weighted sum of the Cu $3s$ and $3p$ levels (which contribute to an $M_{23}VV$ Auger transition) and of the Au $4f$, $5s$, and $5p$ levels (which give rise to the Au lines below 80 eV [13]. The calculated intensity for Cu was normalized to 1 for a clean Cu(100) surface and that for Au was normalized to 1 for 2 ML's of Au.

The most striking thing about the data obtained at 173 K is that the PAES intensity in the Au peak rises so rapidly at low coverage—reaching 40% of the value for a pure gold surface at a coverage of 0.07 ML Au on Cu. Correspondingly, the Cu PAES signal decreases to 60% of the clean surface value at 0.07 ML Au. The clear implication is that those positrons that annihilate with core electrons are seeking out the gold atoms in preference to the Cu atoms. Referring to Fig. 1(a) it can be seen that the calculations, which assume that the positron is delocalized in the surface plane, do not show the degree of low coverage enhancement seen in the experimental results (the experimental results are almost a factor of 2 higher at 0.07 ML). These calculations take into account the fact that the Au atoms are above the Cu plane [16], and are thus more "exposed" to a positron diffusing on the surface. Further, it was not possible to significantly increase the low coverage enhancement by adjustment (within physically reasonable bounds) of the parameters used in the calculation. We note that the same method of calculation did provide good agreement with experiments in which S is deposited on a Cu substrate [8].

Next, let us consider the possibility that the enhancement of the Au signal is due to the localization of positrons on Au islands. An estimate of the island size necessary to produce the observed enhancement of Au PAES intensities at low coverages was obtained as follows. Including contributions to the Au PAES intensity from both islands and isolated Au atoms we write

$$I_{\mathrm{PAES(norm)}} = (F)f + (1-F)\sigma(\theta_d)\,, \qquad (1)$$

where $I_{\mathrm{PAES(norm)}}$ is the PAES intensity normalized to the intensity for a full monolayer of Au, F is the fraction of positrons trapped at the islands, f is the fraction of the trapped positrons which are located over Au atoms, and $\sigma(\theta_d)$ is the normalized PAES intensity calculated assuming a delocalized positron wave function and a coverage, θ_d, of distributed Au atoms. Using the observation that $I_{\mathrm{PAES(norm)}} = 0.4$ at 0.07 ML, and the value $\sigma(0.07\ \mathrm{ML}) \approx 0.14$ [see Fig. 1(a)] we can invert Eq. (1), to find $f = 0.26/F + 0.14$. Taken together with the fact that $0 \le F \le 1$ and $0 \le f \le 1$, this implies that at 0.07 ML, $0.4 \le f \le 1$ and $0.3 \le F \le 1$.

Modeling the island regions using a cylindrically symmetric finite square well potential, ground state solutions to the Schrödinger equation for a single positron were obtained for a range of island radii and well depths. We assume that $f \le f_w(R)$, where $f_w(R)$ is the square of the positron wave function over the well (designated as the "fraction inside the well" in Fig. 2). We can estimate the magnitude of the well depth, E_w, associated with a Au island using the relation $E_w = [E_b(\text{island}) - E_b(\text{substrate})] + [\phi^-(\text{island}) - \phi^-(\text{substrate})]$ where the first expression in brackets represents the differences between island and substrate values of the positron surface state binding energy and the second expression in brackets takes into account the contact potential differences between the two regions. Given that the activation energy for thermal desorption of Ps can be expressed as $E_a = E_b + \phi^- - 6.8$ eV, it is equivalent to write $E_w = E_a(\text{island}) - E_a(\text{substrate})$. The value of E_a for a layer of Au on Cu(100)

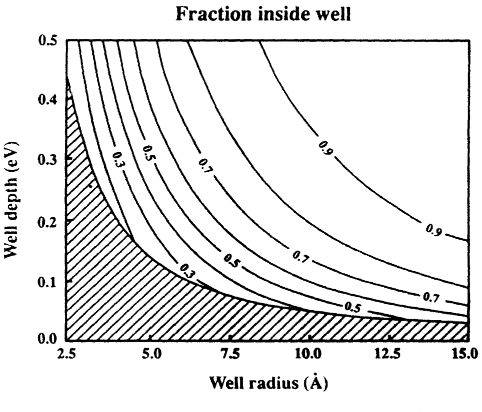

FIG. 2. The calculated fraction of positron density inside a two dimensional square well (indicated on the contour lines) as a function of well radius and depth. In order to simplify calculations, it was assumed that the positron wave function vanishes at a radius of 30 Å. This assumption leads to a failure of the program to find bound states in the shaded region.

has not been measured. However, the known values of E_a for clean metals range from ~ 0.3 eV to ~ 0.7 eV [1] so it is reasonable to assume that $E_w \leq 0.4$ eV. Using this upper bound for E_w, it can be seen from Fig. 2 that the islands must have radii ≥ 4 Å at a coverage of 0.07 ML in order to obtain a value of $f_w(R) \geq 0.4$. The existence of Au islands on the Cu surface is consistent with scanning tunneling microscopy (STM) observations of the formation of islands after submonolayer deposition of Au [17]. Although in the STM case, the deposition was done at room temperature and the islands were reported to consist of Au/Cu surface alloy.

It should be noted that these calculations rule out the possibility that our results can be accounted for in terms of the binding of positrons to single isolated Au atoms. It is not enough that the positron is bound to the Au atom, a large fraction of the positron density must be located within a circle of radius $R < 2$ Å in order to overlap (and annihilate) with the localized core levels of the Au atoms rather than those of the Cu substrate. It is clear from Fig. 2 that this would require an unphysically large amount of energy. Similar arguments rule out the possibility that our results are due to positrons trapped at step edges decorated with a single row of gold [18].

The experimental PAES intensities obtained at 303 K shown in Fig. 1(b) are approximately proportional to the fraction of the top layer occupied by Au atoms and are in general agreement with the values calculated for a mixed alloy layer. It is reasonable that the model calculations should be in better agreement with the data obtained at 303 K than with that obtained at 173 K since effects due to an inhomogeneous distribution of Au (such as islands) would be largely eliminated by alloy formation.

It is interesting to note that the intentional introduction of surface damage by sputtering caused a marked decrease in the low coverage enhancement of the Au PAES intensity sensitivity seen on the annealed sample at low temperatures. The Cu(100) sample was sputtered for 5 min with 3 keV Ne ions at 173 K until the LEED spot profiles were visibly broadened and then Au was deposited on this surface at 173 K. Figure 1(c) shows the PAES intensity for the Au deposited on the sputtered Cu(100) substrate as compared with the PAES intensity for the Au deposited on annealed Cu(100) at 173 K. The Au PAES intensity versus coverage plot for the sputtered Cu substrate is closer to that obtained at 303 K and is in reasonable agreement with the theoretical calculation for a Au overlayer. Possible explanations for the reduction of low coverage enhancement are as follows: (1) A high density of defects prevents the formation of Au islands; (2) the sputter induced defects promote the intermixing of the Au into the Cu layer; (3) the presence of many defects may provide sites at which the positron may localize, which compete with those sites which contain Au atoms.

In this paper we have presented the results of a PAES study of submonolayer films of Au deposited on a Cu(100) surface. The PAES intensity of Au is abnormally large for Au depositions at 173 K at low coverages. This behavior indicates that positrons are annihilating preferentially with the Au overlayer atoms as compared to the Cu substrate atoms. Such preferential annihilation could not be accounted for in model calculations based on delocalized positrons and uniformly distributed Au atoms. The clear implication is that the positron density is concentrated at sites containing Au atoms, most likely Au islands. An effective island size is estimated from model calculations. Large differences between annealed and sputtered surfaces indicate that the degree to which positrons become localized at Au sites is highly dependent on the presence of sputter damage. We also observed that the Au PAES intensity saturates above 1 ML of Au, demonstrating the extremely high top layer selectivity of PAES. At 303 K we observed changes in the PAES intensity corresponding to surface alloying in Au/Cu(100).

This work was supported by the Welch Foundation, the Texas Advanced Research Program, NATO Grant No. 900-649, and NSF Grant No. DMR 9106238.

---

[1] P. J. Schultz and K. G. Lynn, Rev. Mod. Phys. **60**, 701 (1988), and references therein; in Proceedings of the Fifth International Workshop on Low Energy Positron Beams for Solids and Surfaces, edited by E. Ottewitte and A. Weiss, (AIP, New York, to be published).

[2] R. M. Nieminen and M. J. Puska, Phys. Rev. Lett. **50**, 281 (1983).

[3] D. M. Chen, S. Berko, K. F. Canter, K. G. Lynn, A. P. Mills, Jr., L. O. Roellig, P. Sferlazzo, M. Weinert, and R. N. West, Phys. Rev. B **39**, 3966 (1989).

[4] M. F. Crommie, C. P. Lutz, and D. M. Eigler, Science **60**, 218 (1993).

[5] A. P. Brown, K. O. Jensen, and A. B. Walker, J. Phys. F **18**, L141 (1988).

[6] A. R. Koymen, D. W. Gidley, and T. W. Capehart, Phys. Rev. B **35**, 1034 (1987).

[7] Anna Rubaszek, Phys. Rev. B **44**, 10857 (1991).

[8] D. Mehl, A. R. Koymen, K. O. Jensen, F. Gotward, and A. Weiss, Phys. Rev. B **41**, 799 (1990).

[9] R. Mayer and A. Weiss, Phys. Rev. B **38**, 11927 (1988).

[10] A. R. Koymen, K H Lee, G. Yang, and A. H. Weiss, Phys. Rev. B **48**, 2020 (1993).

[11] C. Lei, D. Mehl, A. R. Koymen, F. Gotwald, M. Jibaly, and A. Weiss, Rev. Sci. Instrum. **60**, 3656 (1988).

[12] G. W. Graham, Surf. Sci. **184**, 137 (1986).

[13] K. H. Lee, A. R. Koymen, D. Mehl, K. O. Jensen, and A. Weiss, Surf. Sci. **264**, 127 (1992).

[14] K. Jensen and A. Weiss, Phys. Rev. B **41**, 3928 (1990).

[15] M. Weinert and R. E. Watson, Phys. Rev. B **29**, 3001 (1984).

[16] J. C. Hansen, J. A. Benson, W. D. Clendening, M. T. McEllistrem, and J. G. Tobin, Phys. Rev. B **36**, 6186 (1987).

[17] D. D. Chambliss and S. Chiang, Surf. Sci. **264**, L187 (1992).

[18] K. H. Lee, Ph.D. dissertation, University of Texas at Arlington, 1992.