Positron States on the Cs/Cu(100) Surface

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The attenuation of the Cu $M_{2,3}VV$ Auger peak with Cs coverage on Cu(100) was measured using positron-annihilation-induced Auger electron spectroscopy (PAES) and conventional (electron-induced) Auger electron spectroscopy. The data (obtained at both 303 and 163 K) indicate that below a critical coverage (~0.7 monolayer) the positrons are trapped at the Cu/Cs interface in agreement with theoretical calculations. We observe a sharp (less than 0.02 monolayer wide) drop in the normalized PAES intensity at the critical coverage indicating a transition to another positron state in which the positrons are localized on the vacuum side of the Cs overlayer.

Both electrons and positrons have quantum-mechanical states at surfaces which have no equivalent in the bulk. The binding energies of the surface image state observed for electrons can be interpreted in terms of a simple image potential truncated at the surface [1]. However, modeling of the positron surface state [2] is considerably more complicated since the positrons reside so close to the surface that a simple image potential is inadequate [3]. Direct evidence for positron surface states was provided by the observation that positronium (Ps) could be thermally activated from clean metal surfaces into which positrons had been injected at low energies [4,5]. Analysis of the temperature dependence of Ps emission permits an accurate determination of the activation energy E_a. Recently, the character of the positron surface state has been the subject of much controversy. In particular, two starting points have been suggested for modeling this state: (1) a single (dressed) particle and (2) a positronium atom [6-9].

If the positron is treated as a single charged particle trapped in an image potential well, the binding energy of the positron in the surface state, E_b, can be deduced [4,5] from an energy balance equation [Eq. (1)] appropriate for a Born-Haber cycle:

$$E_a = \phi_- + E_b - \tfrac{1}{2}\mathscr{R} , \qquad (1)$$

where ϕ_- is the electron work function for the surface and $\tfrac{1}{2}\mathscr{R} \approx 6.8$ eV is the ionization energy of ground state Ps. The relatively low values of E_a [for Cu(100), $E_b = 2.77$ eV and $E_a = 0.56$ eV [10]], taken together with Eq. (1), suggest that it should be possible to reduce E_a to zero by using an alkali coverage of ~0.1 monolayer (ML) to reduce ϕ_- and thereby obtain a cryogenic source of Ps with kinetic energies corresponding to room temperature or below. However, in experiments performed by Gidley, Koymen, and Capehart [7] on alkali-metal-covered Ni surfaces it was found that surprisingly large changes in the electron work function were required to reduce E_a (a more than 3-eV decrease in ϕ_- diminished E_a by less than 0.4 eV). Gidley, Koymen, and

Capehart [7] explained the lack of sensitivity of the activation energy to the change in ϕ_- in terms of an effective medium theory [11]. In this model (which is similar to the weakly physisorbed Ps picture of Platzman and Tzoar [6]) Gidley, Koymen, and Capehart assume that the positron is highly correlated with electrons and acts like a neutral Ps-like particle and that Eq. (1), therefore, is not appropriate. Nieminen and Jensen [8] (NJ), however, were able to quantitatively account for the large change in E_b implied by Eq. (1) in detailed calculations of the positron wave function. They found that the same charge rearrangement that leads to the lowering of the electron work function causes the positron to become localized in the region between the substrate and the alkali-metal overlayer producing an increase in the positron binding energy.

In this paper we describe experiments on Cs/Cu(100) using positron-annihilation-induced Auger electron spectroscopy (PAES) [12-14], aimed at testing the validity of the NJ model. In PAES, the energy spectra of Auger electrons emitted following the annihilation of a positron with a core electron provide information about the elemental identity of the atoms near which the positron had been localized [14]. Thus if the positron is trapped between the Cs and the Cu then the PAES Cu signal should remain close to the clean-surface value after deposition of Cs. If it is not trapped at the interface, we would expect the positron wave function to be pushed away from the Cu by the presence of the Cs overlayer and therefore that the signal from the Cu will decrease rapidly as is the case for S on Cu [14]. We found, in fact, that our results are consistent with the NJ model only up to a critical coverage corresponding to ~0.7 ML. An important result of this study is the discovery that the PAES intensity drops sharply almost to zero at the critical coverage. This result deviates significantly from the predictions based on the NJ model and is indicative of the positron making a transition to a state in which it is no longer localized in the Cs/Cu interface.

The PAES measurements were performed using the

UHV magnetically guided positron-beam–surface system at the University of Texas at Arlington which has been described previously [13]. Electron-simulated Auger spectroscopy (EAES) measurements were performed using the same spectrometer to obtain EAES spectra with the same geometry as used in the PAES measurements. A single-pass cylindrical mirror analyzer (CMA) was used in routine EAES measurements. Three NaI(Tl) scintillators detected annihilation gamma rays emitted in coincidence with Auger electrons. The Cu(100) surface was cleaned by repeated cycles of 2-keV Ne$^+$ ion sputtering and annealing at 923 K for 10 min.

All Cs deposition was performed at room temperature using resistively heated SAES Cs getters. The Cs coverage was determined by using the CMA to measure the ratio (R) of Cs (563 eV) EAES Auger peak to Cu (920 eV) peak and by observation of the evolution of the LEED pattern. At room temperature, saturation coverage of Cs on Cu(100) is 1 physical ML. A hcp LEED pattern due to the Cs overlayer appears at 0.8 ML and is completed by 1.0 ML [15,16]. Extreme care was taken with respect to surface cleanliness. The base pressure in the chamber was $< 2\times 10^{-10}$ Torr. The change in electron work function ($\Delta\phi_-$) as a function of Cs coverage was measured by determining the sample voltage at which the positron beam was reflected [17]. The results shown in Fig. 1(c) agree well with previous measurements [15].

The Ps fraction (f_{Ps}) was measured by analyzing the pulse-height spectrum from a NaI γ-ray detector [4]. The Ps fraction as a function of Cs coverage for both 303 and 163 K are shown in Fig. 1(b). Isothermal (303 K) desorption of positrons as Ps from the Cs/Cu(100) system occurs after ϕ_- has dropped by 3 eV (at $\sim$0.5 ML Cs) as shown in Figs. 1(b) and 1(c). This result is consistent with previous measurements for alkali metals on Ni surfaces [7].

The decrease in the positron-annihilation-induced Cu $M_{23}VV$ ($\sim$60 eV) Auger signal (normalized to the clean-Cu value), I_{PAES}, correlates very strongly with f_{Ps} as shown in Figs. 1(a) and 1(b). At room temperature, I_{PAES} drops to zero as f_{Ps} rises to $\sim$100% for coverages larger than $\sim$0.5 ML Cs ($R = 0.07$). On the other hand, as shown in Fig. 2(c) the EAES derivative peak-to-peak intensity (normalized to the clean-Cu EAES intensity), I_{EAES}, decreases linearly to a finite value at 1 ML Cs coverage. It can also be seen in Fig. 1(a) that the point at which I_{PAES} drops most sharply (and correspondingly the Ps fraction increases most rapidly) shifts out to higher coverage as the temperature is lowered from 303 to 163 K. In addition the f_{Ps} saturates at a much lower value ($\sim$70%). At the coverages where f_{Ps} is changing rapidly, the low-temperature suppression of Ps desorption causes a corresponding increase in the Cu PAES signal. This would not be the case if the positrons desorbing as Ps were not trapped in a state localized at the Cs/Cu interface.
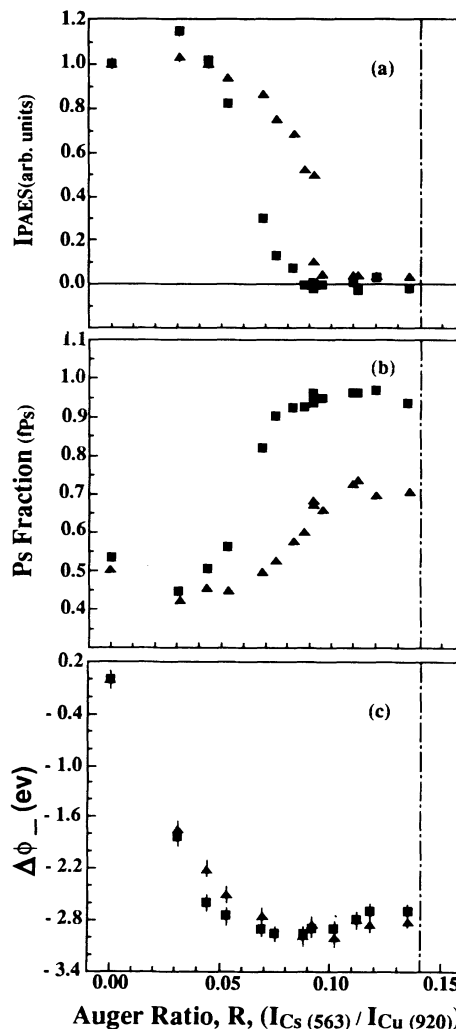

FIG. 1. (a) The Cu $M_{23}VV$ PAES intensity I_{PAES} (normalized to the room temperature value for clean Cu), (b) positronium fraction f_{Ps}, and (c) change in electron work function, $\Delta\phi_-$, as a function of the ratio of the Cs (563 eV) to the Cu (920 eV) Auger peaks (R). The Cs coverage is approximately proportional to R. A ratio of 0.14 (indicated by the vertical dash-dotted line) corresponds to 1 physical ML. Data were obtained both at 303 K (squares) and at 163 K (triangles).

If we assume that the I_{PAES} is proportional to the fraction of positrons, f_{ss}, that annihilate in the surface state multiplied by the probability $P(M_{23}VV)$ that a positron trapped in the surface state annihilates with a core electron resulting in the emission of the relevant Auger electron, we can write

$$P(M_{23}VV) \sim I_{PAES}/(1-f_{Ps}) , \qquad (2)$$

where we have used the fact that for positrons incident at low energies on a negatively biased Cu surface [18] the quantity f_{ss} can be found to a very good approximation from the expression

$$f_{ss} = 1 - f_{Ps} . \qquad (3)$$
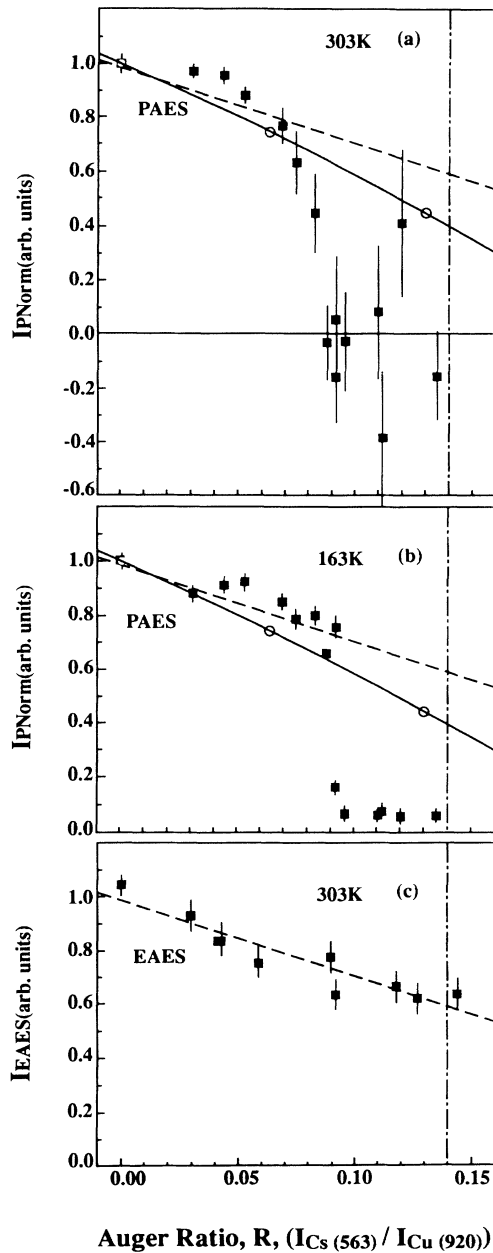
Hence the PAES intensity normalized to the fraction of

Auger Ratio, R, ($I_{Cs\,(563)}$ / $I_{Cu\,(920)}$)

FIG. 2. $I_{P\,norm}$ [$I_{PAES}/(1-f_{Ps})$], at (a) 303 K and (b) 163 K, and (c) the EAES intensity I_{EAES} as a function of R. The reason that some of the data points in (a) go below zero is because a small constant background has been subtracted from I_{PAES} which is very close to zero at high Cs coverage. This effect was exaggerated by dividing by $1-f_{Ps}$ which is also close to zero at high coverage. The dashed line shown in (a)-(c) was determined from a least-squares fit to the EAES data shown in (c). The solid line in (a) and (b) is a parabola fit to the values of the PAES intensity calculated for three different coverages of Cs on Cu using the NJ model (open circles). The vertical dash-dotted line indicates the value of R corresponding to 1 physical monolayer. The fact that we obtained two widely different values for $I_{P\,norm}$ at $R=0.092$ provides an indication of both the sharpness of the transition and the uncertainty in determining R.

positrons in the surface state, $I_{P\,norm}=I_{PAES}/(1-f_{Ps})$, which is plotted as a function of Cs coverage in Figs. 2(a) ($T=303$ K) and 2(b) ($T=163$ K), can be used to determine the Cs coverage dependence of $P(M_{23}VV)$. I_{EAES} is also shown (dashed line) for comparison. At 163 K, the decrease in $I_{P\,norm}$ is similar to the decrease in the I_{EAES} for Cs coverage up to 0.7 ML ($R=0.092$). The fact that the decrease in $I_{P\,norm}$ between 0 and ~0.7 ML is similar to the small decrease observed in I_{EAES} indicates that most of it is due to inelastic scattering (which should be similar to that in EAES) and not to a decrease in the Cu core annihilation probability. This is in contrast to the results for a S overlayer on Cu [14] in which $I_{P\,norm}$ decreased 4 times faster than the EAES intensity as a function of S coverage. This decrease, in the case of S on Cu, is due to the fact that the S overlayer pushes the positron wave function away from the Cu ion cores [14]. For Cs coverages greater than 0.7 ML at 163 K (0.5 ML at room temperature), $I_{P\,norm}$ deviates from the linear attenuation behavior and rapidly drops to zero indicating a sharp change in the amount of overlap of the positron wave function with the Cu substrate. The error bars in $I_{P\,norm}$ in the room-temperature measurements become very large for the higher coverages due to fact that the percent error in $1-f_{Ps}$ grows very rapidly as f_{Ps} becomes close to 1. To make sure that the sharp drop in $I_{P\,norm}$ observed at room temperature was not due to systematic errors introduced by calibration of f_{Ps}, the measurements were repeated at 163 K. In this case f_{Ps} saturates at $\sim70\%$ and systematic errors in determining f_{Ps} ($\pm5\%$) are not large enough to produce the kind of behavior observed in Fig. 2(a).

Theoretical calculations [19] of $P(M_{23}VV)$ (multiplied by an attenuation factor determined from the attenuation of the EAES intensity) are shown in Figs. 2(a) and 2(b) for comparison with the measured values of $I_{P\,norm}$. In these calculations, the image-potential-induced positron surface state wave function was found by numerical solution of a single particle Schrödinger equation. The potential was calculated using the corrugated mirror model [20,21]. For Cs coverages of 0.46 and 0.92 physical monolayers, the calculations indicate that the positron density peaks in a plane about halfway between a plane passing through the Cs cores and a corresponding plane through the Cu cores. After calculation of the positron wave function, the annihilation rates $\lambda_{n,l}$ for different electronic levels were calculated using the independent particle model (IPM). The annihilation probabilities $p_{n,l}$ are obtained by dividing $\lambda_{n,l}$ by the total annihilation rate, which is calculated using the local density approximation with the local rate in the image potential region set to zero [22]. The predicted core annihilation probabilities are very small for the Cs core levels. The two highest probabilities are 0.020% for 4p and 0.068% for 4d as compared to 3.0% for the 3p level of Cu [19]. This is consistent with the fact that no PAES signal from the Cs overlayer is evident in the experimental spectra.

The theory and experiment are in reasonable agreement below the critical coverage of ~ 0.7 ML, suggesting that the NJ picture of trapping at the Cs/Cu interface is qualitatively correct. However, the present theory cannot reproduce the sharp drop in $I_{P\,norm}$ observed experimentally at ~ 0.7 ML. The implication of the experimental results is that there is a transition from the state at the Cs/Cu interface to a state in which the positron is pushed to a position outside the Cs overlayer into the vacuum at the critical coverage. It can be seen by comparing the data shown in Figs. 2(a) and 2(b) that the drop in $I_{P\,norm}$ is sharper at 163 K than at 303 K. This may be an indication that both the interface state and surface trapped state coexist with a small energy difference and that at higher temperature the positron can be excited into the surface trapped state at lower Cs coverages. The sharper transition might also be an indication that the Cs is more uniformly distributed at low temperatures. Previous LEED studies [16] for this system suggest that the Cs overlayer is disordered at room temperature (below 0.8 ML) while the Cs is uniformly spaced at low temperature (~ 150 K). The behavior of $I_{P\,norm}$ below the critical coverage could not be due to physisorbed Ps [6] since Ps cannot exist at the electron densities present at the Cs/Cu interface [23].

Note that the critical coverage corresponds to the point at which the electron work function reaches its minimum. Recent theoretical [24] and experimental [25] work indicates that the slight increase in the electron work function at higher alkali-metal coverages is mostly due to the decrease of the charge depletion on the vacuum side of the alkali-metal overlayer. The sharp drop in $I_{P\,norm}$ above the critical coverage may be caused by this charge relocation in the Cs overlayer.

In conclusion, the fact that, at coverages of less than 0.7 physical ML, an overlayer of Cs does not lead to the large decrease in PAES signal seen with other overlayer systems (e.g., S/Cu [14]) is consistent with the hypothesis that positrons become trapped at the Cs/Cu interface as predicted in the NJ model. However, the NJ model fails to account for a sharp transition in the normalized PAES intensity at a critical Cs coverage. The sharp drop in PAES intensity suggests a transition to another positron state localized on the vacuum side of the Cs overlayer. This transition cannot be accounted for from calculations performed to date. The origin of this transition may reflect changes in the electronic distribution or structural rearrangement of Cs atoms at the surface.

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