# Observation of defects associated with the Cu/W(110) interface as studied with variable-energy positrons

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Positron emission from a W(110) single crystal has been studied as a function of copper coverage utilizing a variable-energy positron beam in conjunction with low-energy electron diffraction and Auger-electron spectroscopy. Evidence is presented that indicates that significant positron localization occurs at defects associated with the Cu/W(110) interface, which can be removed by high-temperature annealing. Our data also reveal new information about the islanding of copper on tungsten, providing a reliable means of identifying and quantifying the relative two-dimensional coverage of the surface by these islands.

#### I. INTRODUCTION

Measurements of the electron work function  $(\phi_{-})$  have been one method used in past years to gain insight into the electronic properties of metallic surfaces. The application of this technique to the study of adsorption on clean surfaces has yielded semiquantitative information about surface coverage, surface diffusion, etc. An overview has been presented by Hölzl *et al.*<sup>1</sup>

It has recently become possible to complement the more conventional studies of  $\phi_{-}$  with measurements of the *positron* work function  $\phi_{+}$ , provided that  $\phi_{+}$  is negative. The possibilities of this complementary technique have not as yet been fully explored because it is new and relatively difficult; however, it is already clear from several studies that new information can be obtained from these measurements.<sup>2-18</sup>

This paper represents the first application of the "slow-positron" technique to the study of interfaces. Results are presented for measurements of  $\phi_+$  and reemitted positron yield for evaporated Cu on W(110), which were augmented at various stages with low-energy electron diffraction (LEED) and Auger electron spectroscopy. The data confirm earlier findings  $^{19-21}$  that a transitional layer is formed prior to the epitaxial growth of Cu(111) on the W(110) substrate. Coincident with the formation of this layer the otherwise "freely" diffusing positrons were localized in open-volume defects, most likely associated with the first few monolayers of copper. It was possible to remove the defects while only partially desorbing the Cu by annealing a relatively thick overlayer (tens of monolayers) to  $\sim 1225$  K. The similarity of this temperature to the 1200 K threshold previously determined<sup>21</sup> for the first binding state of Cu on W(110) suggests that thermal activation of the first monolayer is required to fully remove the damage. In addition we find clear evidence for islanding of the Cu on W(110) that follows heat treatment of the as-evaporated system. The positron technique appears to allow a direct quantification of the relative patch areas for this system that is not so straightforward using other techniques.

#### **II. EXPERIMENTAL CONSIDERATIONS**

The variable-energy positron apparatus and associated ultrahigh-vacuum (UHV) surface chamber used for these studies have been described fully elsewhere.<sup>22</sup> Positrons emitted from a <sup>58</sup>Co source  $(\sim 100 \text{ mCi})$  are "moderated" to thermal energies by a well-characterized metallic single crystal [usually Cu(111) + S] used in a backscattering geometry. This process involves the implantation, thermalization, and subsequent diffusion of the positrons within the moderator. Those that diffuse back to the surface can be reemitted into the vacuum with kinetic energy characteristic of  $|\phi_+|$ , provided that  $\phi_+$  is negative. A conversion efficiency of  $\epsilon \approx 1 \times 10^{-3}$  for Cu can be attained under highvacuum conditions. The reemitted positrons  $(\sim 7 \times 10^5$  per sec) are transported through the beam tube along the axis of a guiding magnetic field and electrostatically accelerated to any desired energy within the 0-7 keV range. The operating pressure in the chamber was about  $5 \times 10^{-10}$  Torr throughout the experiment, rising to about  $1 \times 10^{-8}$  Torr during Cu evaporation (measured directly below the evaporator-see Fig. 1).

When a positron enters the target specimen it will rapidly thermalize at mean depths on the order of

27

6626

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FIG. 1. UHV target chamber is shown to demonstrate the general arrangement of the various components. The incident positron beam follows the central axis of a magnetic field ( $\sim 100$  G) generated by a series of 28-in. diam. split solenoids (not shown).

50 Å per keV of incident energy, and begin to diffuse through the crystal. The possible fates include the following:

(1) Annihilation from a freely diffusing state within the metal ( $\tau \approx 10^{-10}$  sec) or from a localized state in bulk or interfacial defects ( $\tau \approx 2 \times 10^{-10}$  sec).<sup>3</sup>

(2) Localization and subsequent annihilation in a two-dimensional surface state ( $\tau \approx 4 \times 10^{-10}$  sec).<sup>23,24</sup>

(3) Thermal desorption from the surface state at relatively high specimen temperatures as a positronium (Ps) atom, which is the electron-positron bound state.<sup>4</sup>

(4) Direct emission as a neutral Ps atom<sup>5</sup> or Ps<sup>-</sup> ion.<sup>6</sup>

(5) Direct reemission as a free positron provided that  $\phi_+$  is negative.<sup>7</sup>

Information about the annihilating positrons is usually deduced from a simple analysis of the annihilation  $\gamma$ -ray energy spectrum, and in some cases from the time of decay. One commonly measured parameter is the relative fraction F of incident positrons that are emitted as positronium. F is derived from the relative fraction of total counts that fall in the 511-keV photopeak.<sup>8</sup> The dependence of either F or the yield of reemitted positrons on incident positron energy can lead to an estimation of the mean positron diffusion length in the specimen.<sup>5,8</sup> These data as a function of specimen temperature can also lead to information about bulk, overlayer, and interfacial defect concentrations.<sup>8,10</sup>

In this paper we determine the reemitted positron yield  $Y_1$  and positron work function  $\phi_+$  from measurements of the total count rate of positrons annihilating at the target as a function of bias on a pair of nearby retarding grids (see Fig. 1). Those positrons which either annihilate in the specimen or are reemitted *and* retarded by the grids are detected in the total rate, whereas those that pass through the grids without annihilating are not. Owing to the magnetic field along the positron beam axis we measure only the normal component of the reemitted positron energy.

The integral yield distributions which are described in detail in the following section (see Fig. 2) are obtained from the raw data (count rate versus bias) by scaling and offsetting so that the plotted values range from the measured yield  $Y_1$  for small bias to zero for large bias. On occasion, as in Fig. 3, a set of measurements is plotted normalized to unity to facilitate comparison. The yield is calculated by dividing the overall change in rate from small bias to large by the maximum rate (at small bias). In this calculation, three corrections are relevant:



FIG. 2. Typical integral distribution of reemitted positron yield vs sample bias is shown for W(110), as obtained with a beam of 2-keV incident positrons. The "net" zero of the abscissa (labeled  $E_1$ ) is the difference between the contact potentials of the target specimen ( $\phi_{-}$ ) and retarding grids ( $\phi_g$ ) (Ref. 2). The positron work function  $\phi_+$  is defined as the difference between this point and the point ( $E_3$ ) indicating the energy with which most of the positrons are reemitted. The linear tail between  $E_1$  and  $E_2$  is ascribed to inelastic energy-loss processes at the surface (Ref. 12).

(1) A constant fraction of the incident positrons will annihilate from bulk or surface states, or as reemitted Ps. This leads to a countrate that is independent of sample bias (flat background).

(2) Incident and reemitted positrons have approximately a 19% probability of annihilating in the retarding grids, as determined by optical transmission measurements. This leads to a background which has the inverse shape to the distribution itself, being twice the intensity for *reemitted* positrons which pass through the grids (sample bias greater than  $E_1$ ; Fig. 2) than for those that do not (sample bias less than  $E_3$ ). The magnitude of this correction is adjusted for the relative efficiency of detection as based on simple geometrical considerations.

(3) A correction could also be made to the maximum rate to account for the differing detection efficiency for positrons which form o-Ps in the sample from that for positrons which form p-Ps or annihilate directly. This detection efficiency is made larger by the 3:2 ratio in number of emitted photons, but smaller by the larger distance traveled by o-Ps with its resultant decrease in detection solid angle. As this correction is thus expected to be small, it is



FIG. 3. Integral distributions of reemitted positron yield vs bias are shown for the various stages of the Cu/W(110) system discussed in the text. The data are normalized to facilitate comparison of the features. The total yields for the above curves are the following: (a)  $Y_1 \approx 33\%$ , (b)  $Y_1 \approx 12\%$ , (c)  $Y_1 \approx 10\%$  for the as-deposited system ( $\bullet$ ) and  $Y_1 \approx 28\%$  for well-annealed system (+), and (d)  $Y_1 \approx 25\%$  (see Table I).

neglected here.

In addition to the positron measurements the surface was characterized at various times with LEED and 4-grid retarding-field Auger electron spectroscopy (AES). Values quoted for AES results in this report are expressed as sensitivity-corrected<sup>25</sup> peak amplitudes  $(A_A)$  relative to tungsten  $(A_A = 1)$ , except those for Cu which are expressed as approximate fractions of a monolayer of surface coverage [where  $\Theta = 1$  corresponds to one monolayer—approximately  $14 \times 10^{14}$  cm<sup>-2</sup> (Ref. 21)]. The sample was mounted on a polycrystalline W foil which could be resistively heated with electric current. Temperatures were measured with a Pt-Pt-Rh thermocouple that was checked at  $\sim 1000$  °C with an optical pyrometer. The W(110) crystal measured  $1 \times 0.4 \times \frac{1}{8}$  in. and was mechanically polished to a mirror finish and treated by the supplier prior to annealing to reduce interstitial C impurities.<sup>26</sup> Even after this treatment it was found that each flash heating of the specimen in vacuum (to  $\geq$  1500 °C for 2 min) caused C to migrate to the surface  $(A_A \approx 0.2)$  which was largely removed by subsequent heating at ~500 °C in ~ $10^{-8}$ Torr of oxygen.<sup>27</sup> The oxygen was then desorbed by heating the specimen to 1000 °C; no further C contamination of the surface was observed at this temperature.

### **III. CHARACTERISTICS OF THE DATA**

The potential for a thermalized positron inside the metal relative to the vacuum level is a combination of the positron chemical potential  $(\mu_+)$  and the surface dipole (D) which yields a general expression for the positron work function<sup>23,28</sup>:

$$\phi_{+} = -D - \mu_{+} \quad , \tag{1}$$

where  $\mu_+$  is the sum of contributions due to electron-positron correlation  $(E_{\rm corr})$  and repulsion from the ion cores (usually termed the positron zero-point energy  $E_0$ ). The positron-electron correlation for a positron outside the metal gives rise to an "image" potential, which leads to a minimum near the surface that is able to localize the positron.<sup>4,23</sup> The definition of  $\phi_+$  is analogous to that for the electron work function,

$$\phi_{-} = D - \mu_{-} \quad . \tag{2}$$

The above definitions imply that surface changes (involving *only* the dipole *D*) would be reflected equally in  $\phi_{-}$  and  $\phi_{+}$ , as was demonstrated experimentally for Cu by Murray *et al.*<sup>2</sup>

The relationship of  $\phi_+$  and  $\phi_-$  to the energy dependence of the integral yield of reemitted positrons is illustrated in Fig. 2. The point labeled  $E_1$  in Fig. 2 represents the retarding bias at which all reemitted positrons can escape through the grids. This is the difference between the contact potentials for the target specimen  $(\phi_{-})$  and retarding grids  $(\phi_{\alpha})^2$  The majority of the positrons that are reemitted have energy  $e\phi_+$  and are sharply peaked in a direction that is normal to the crystal surface.<sup>11</sup> Because of this the integral (normal) energy distribution shows the maximum decrease when the net sample bias is  $\phi_+$  (point  $E_3$  in Fig. 2). The point  $E_3$ (equal to  $\phi_+ + \phi_- - \phi_g$ ) is usually measured by taking the position of the maximum value of the differential energy distribution, such as that shown in Fig. 4(a). The width of this peak is mainly due to the Gaussian filter used to smooth the data prior to differentiation, although it also includes contributions from the positron's thermal energy, the resolution of the retarding grids and, to some extent, a broadening introduced by positrons being reemitted before complete thermalization. The linear portion of the curve between  $E_1$  and  $E_2$  in Fig. 2 has recently been ascribed to inelastic processes at the crystal surface.<sup>12,13</sup> It is possible that this "tail" in the distribution could arise from elastic scattering of the positrons into off-normal angles, which would not cause a reduction in the total kinetic energy of the reemitted positrons. However, preliminary results from a study of the total energy of reemitted positrons using a fully electrostatic positron beam<sup>14</sup> indicate that a significant portion of this tail is likely associated with a net loss of total energy. The relative

TABLE I. The parameters defined on Fig. 2 are listed for the data presented in Figs. 3 and 4, together with the positron work function  $(\phi_+=E_3-E_1)$ . The inelastic fraction is expressed as a percent of the absolute yield  $(Y_1)$ .

	<i>E</i> <sub>1</sub> (V)	<i>E</i> <sub>3</sub> (V)	$\phi_+$ (eV)	$egin{array}{c} Y_1 \ (\%) \end{array}$	Inelastic fraction (%)
(a) W(110)	$+0.18\pm0.15$	$-2.78\pm0.1$	$-2.96 \pm 0.2$	33	30
(b) Low Cu coverage	$+0.23\pm0.15$	$-2.38 \pm 0.1$	$-2.61\pm0.2$	12	70
(c) $Cu(111)/W(110)$	$+0.50\pm0.15$	$-0.14{\pm}0.1$	$-0.64\pm0.2$	10/28	< 10
(d) Cu islands on W(110)	$+ 0.28 \pm 0.15$	$-2.63 \pm 0.1$ $-0.17 \pm 0.1$	$-2.81\pm0.2$ $-0.45\pm0.2$	25	< 10



FIG. 4. Differential distributions for the data in Fig. 3 are shown in this figure. The data in Fig. 3 were smoothed with a Gaussian filter ( $\sigma = 0.33$  V) prior to differentiation. Table I lists the peak positions ( $E_3$  as defined in Fig. 2) for the various curves shown here.

area of the inelastic tail seems to vary depending on the surface condition of the sample.

In any systematic study of reemitted positron distributions (i.e., one in which two or more measurements are made under identical experimental conditions) there is generally useful information contained in the relative positions of the points  $E_1$  and  $E_3$ (Fig. 2), independent of the more easily interpreted determinations of absolute yield  $(Y_1)$ . For example, a change in the surface dipole coupled with constant chemical potentials would be observed as a shift in  $E_1$ , while  $E_3$  remained fixed [from Eqs. (1) and (2)]. This was the case observed for submonolayer adsorption of sulphur on Cu,<sup>2</sup> and would be expected if one were to sequentially measure different faces of one crystal. On the other hand, simple algebra based on Eqs. (1) and (2) demonstrates that shifts in  $E_3$  are evidence of bulk phenomena, viz,

$$\Delta E_3 [\equiv E_3(b) - E_3(a)] = -(\Delta \mu_+ + \Delta \mu_-) , \qquad (3)$$

where a and b refer to any two configurations under comparison. Such shifts were first discussed in relation to a study of the temperature dependence of  $\phi_+$ for Cu(111).<sup>12</sup> This is of particular interest with reference to the tradition of establishing the surface dipole through calculations of the chemical potential,<sup>1,23,28-32</sup> since it provides a rare experimental check on these calculations. This will be discussed further in the following section.

# **IV. DISCUSSION OF RESULTS**

Reemitted positron distributions obtained using 2-keV incident positrons are shown in Fig. 3. The previously defined points  $E_1$  and  $E_3$  (and the corresponding work functions) are tabulated for the various curves in Table I. The response for W(110) that was shown in Fig. 2 is repeated for comparison in Fig. 3(a). Prior to each measurement for clean W(110) the specimen was heated for several minutes in oxygen as previously described. However, there always remained evidence of C ( $A_A < 0.1$ ) as well as traces of S ( $A_A < 0.05$ ) on the surface. Repeat measurements of the distribution shown in Fig. 3(a) revealed that the yield of reemitted positrons  $(Y_1)$ ranged from 25% to 35%. This is slightly lower than the yield of 40% reported by Wilson and Mills<sup>15</sup> for W(111) as studied with 1-keV incident positrons. The differential energy distribution for the curve shown in Fig. 3(a) is presented in Fig. 4(a). The positron work function for W(110) was found to be  $\phi_{\pm} = -2.94 \pm 0.2$  eV (Table I) as compared with  $\phi_{\pm} = -2.64 \pm 0.1$  eV for W(111).<sup>15</sup> The suggestion that  $\phi_+$  and  $\phi_-$  are directly correlated is supported by the above values for  $\phi_+$  when they are compared with appropriately chosen values for the electronwork function, such as  $\phi_{-}=5.25\pm0.02$  eV for W(110) (Ref. 33) and  $\phi_{-}=4.83\pm0.38$  eV for W(111).<sup>34</sup> However, there is sufficient discrepancy in the published values for  $\phi_{-}$  (see, for example, work listed in Ref. 1) to discourage any detailed comparison of  $\Delta \phi_{+}$  and  $\Delta \phi_{-}$ .

As mentioned previously, the approximately linear portion of the distribution pictured in Fig. 2 (between  $E_1$  and  $E_2$ ) is thought to be evidence of inelastic scattering at the surface.<sup>12,13</sup> The relative height of the intersection of the linear tail with the steeper, "narrow-beam" portion of the curve would indicate that approximately  $30\pm5\%$  of the reemitted positrons are inelastically scattered for W(110), which is similar to that observed for W(111).<sup>15</sup> Materials with small positron work functions that have been studied [such as Cu (Refs. 2 and 12)] generally show much smaller (less than 10%) inelastic tails. The relatively large fraction observed for W may be characteristic of materials with large negative positron work functions, although the only other "large work-function" sample with a well-characterized surface that has been studied with positrons is Cr(100).<sup>13</sup> A large inelastic fraction for materials with more negative work functions can be explained by the existence of a larger number of available final states for electrons to be scattered into by the positron while escaping through the metal-vacuum interface.

Figure 3(b) shows a distribution which is typical of a low-coverage evaporation of Cu on the W(110)surface. AES measurements established relative peak amplitudes for Cu:W of 60:40. On the basis of the detailed measurements of Bauer et al.,<sup>21</sup> this would indicate that  $\Theta \approx 1.5$  Cu for this particular set of data. The positron yield of  $y_1 \approx 12\%$  (Table I) is unusually low, indicating significant positron trapping in open-volume defects. Several studies<sup>19-21</sup> have observed a [110] satellite LEED pattern in the early stages of Cu deposition on W(110)interpreted<sup>20</sup> as double-scattering between a strained Cu(111) monolayer and the substrate. Recent evidence<sup>21</sup> indicates that the strain is associated with the second adsorbed monolayer of Cu, the first being constrained to the periodicity of the substrate. It is suggested that the defects observed in the present study arise from incomplete coverage of the first monolayer, although the actual fraction of "vacant" sites may be sufficiently small to be unobservable by other techniques. The diffuse nature of a thermalized positron contributes to its sensitivity to very low levels of defects ( $\sim 0.1$  ppm for monovacancies).<sup>3</sup>

At present it is impossible to unambiguously determine whether the defects are caused by surface impurities or not. It has been shown<sup>35</sup> that contamination of the surface can suppress monolayer-bymonolayer growth of the overlayer leading, in some instances, to agglomeration into island films.<sup>36</sup> This is known not to be the case in the present study both by the sharpness of the LEED spots observed for thicker Cu(111) films and, more definitively, by the absence of the double-stepped reemitted positron distribution that is characteristic of islanding [Figs. 3(d) and 4(d), discussed later in this section]. It is also significant that no additional impurities were introduced during the evaporation process; after each evaporation AES was used to check for C, O, and S, and in all the contamination was below easily detectable limits ( $A_A < 0.01$ ).

The low-coverage data also show a slightly less negative positron work function than was found for clean W(110) (Table I). The results of Bauer *et al.*<sup>21</sup> and Polanski and Sidorski<sup>37</sup> show that copper evaporated on W(110) and W(100) results in a lowering of the electron work function. The former of these two studies<sup>21</sup> shows that a minimum is obtained for  $\phi_{-}$  at about  $\Theta = 1.5$ , yielding a value very near that for Cu(111). It is clear from our results (summarized in Table I) that  $\phi_{+}$  is still much closer to the value for W(110) than it is to Cu(111). This suggests that the positron chemical potential ( $\mu_{+}$ ) changes in a different way than  $\mu_{-}$  as a function of coverage.

It is worth noting that there is an important difference between  $\mu_{+}$  and  $\mu_{-}$ , particularly as related to the special case of adsorbed overlayers. When two metals are brought together the Fermi levels  $(\mu_{-})$  come into coincidence by a momentary flow of charge, and the electrons of both metals come to a common equilibrium. The concept of a Fermi level is inappropriate for a positron since there is never more than one in the sample at any one time, and its interaction with the metal is restricted to a relatively local environment. As a result, the positron does not come into equilibrium with the overlayer until passing through the metal-metal interface. This fundamental difference between  $\mu_{+}$  and  $\mu_{-}$  makes the quantitative comparison between changes in  $\phi_+$ and  $\phi_{-}$  inherently more difficult.

A distinctive feature of the distribution shown in Fig. 3(b) is the large inelastic tail ( $\sim 70\%$ ), also seen as a marked increase in the width of the corresponding differential energy distribution [Fig. 4(b)]. The probability of a positron losing energy over a potential minimum is increased by both the time spent over the well and the depth of the well.<sup>12,23</sup> We attribute the increased inelastic scattering of positrons for this surface to a combination of an effective widening of the "image" potential minimum relative to that found at the surface of clean W(110), and to the presence of pointlike defects in the thin overlayer.

For more than a few monolayers of evaporated copper the precise coverage was not known. However, we have extrapolated the low-coverage evaporation rates (as based on relative Auger amplitudes<sup>21</sup>) to obtain a rough quantitative measure of coverage. The sticking coefficient is not expected to change as a function of coverage. As before, the overlayer always revealed sharp LEED spots characteristic of a smooth Cu(111) surface, and AES indicated no signal for W, C, S, or O  $(A_A < 0.01)$ . The reemitted positron distribution for this system [shown in Fig. 3(c)] is quantitatively similar to that obtained with a clean Cu(111) single crystal.<sup>11</sup> The work function for Cu(111) corresponding to Figs. 3(c) and 4(c) was usually about  $-0.5^{+0.2}_{-0.1}$  eV in agreement with Ref. 11, although in some instances of either relatively low coverage ( $\Theta < 10$ ) or excessive heat treatment it was as large as -1.1 eV. This is likely related to the change in electron work function from the value for W(110) to that for Cu(111) that is found for low coverage.<sup>21,37</sup>

The yield of reemitted positrons for the copperon-tungsten system as deposited was about 10%-15% for evaporations ranging from  $\Theta \approx 15$  to  $\Theta \approx 60$ , which is lower than is typically found for single crystals of Cu(111) by about a factor of 2.<sup>12</sup>

This value was not improved significantly by evaporating on a hot ( $\sim$ 700 K) tungsten substrate, or by annealing the Cu/W(110) system to  $\sim 1125$  K. Since dislocation loops and vacancy clusters in bulk copper are known to recover during annealing at  $\sim 600$  K,<sup>38</sup> these results support the conclusion that defects associated with the Cu/W(110) interface were responsible for the unusually low yields. Consistent with this view it was observed that  $Y_1$  was strongly dependent on incident positron energy  $(E_i)$ for a system in which the extrapolated thickness of the copper overlayer was approximately  $\Theta = 15$ ; a dependence that is not observed for well-annealed, single crystals of either W or Cu.  $Y_1$  dropped from  $15\pm1\%$  over the range  $E_i=0.5-1$  keV to about  $9\pm1\%$  over the range  $E_i = 1.5-2$  keV. Assuming a mean implantation depth of 37  $Å/kV^{n}$ ,<sup>17</sup> where n = 1.6,<sup>18</sup> then the observed decrease in yield occurs when positrons are implanted (on average) between 35 and 70 Å.

It was possible to remove the defects by annealing a thick overlayer ( $\Theta \approx 50$ ) at ~1225 K for between 2 and 4 min. This treatment reproducibly resulted in a yield of between 25% and 28% (at 2-keV incident energy), with the characteristic shape of Cu(111), as illustrated in Fig. 3(c). Two curves are shown in Fig. 3(c); one representing the as-deposited Cu(111) on W(110) with a low yield ( $Y_1 \approx 10\%$ ) and the other representing the annealed Cu-W system, where the yield increased to  $Y_1 \approx 28\%$ . Both curves were normalized by the same amount in order to clearly demonstrate the change introduced by annealing. It can be seen that the only observable difference between the distributions (outside of the large change in yield) is the evidence for a slightly larger inelastic tail after annealing. Thermal desorption studies<sup>21</sup> (TDS) have shown that there are two distinct binding states for Cu/W(110). More specifically it was shown that the first binding state (which corresponds to coverages up to  $\Theta = 1$ ) was desorbed over the temperature range 1200-1300 K, whereas the second ( $\Theta > 1$ ) extended from ~1100-1200 K. The two peaks were separated by a well-defined minimum at  $\sim 1200$  K. The fact that it was necessary in the present study to heat the overlayer above 1200 K suggests that the defect recovery involved a physical rearrangement of the first monolayer. This is consistent with the model previously mentioned that vacant sites are left in the first (commensurate) layer during deposition.

In Sec. III the relationship between shifts in  $E_3$  (Fig. 2) and bulk chemical potentials were discussed. Since this study provides a systematic transition from W(110) to Cu(111) [curves 3(a) and 3(c), 4(a) and 4(c), and Table I], it is useful to compare the results with theory. Table II lists a compilation of recent calculations of both  $\mu_+$  and  $\mu_-$ , together with the results of the present study and of an independent study by Wilson and Mills<sup>15</sup> involving measurements on Cr(100) and Al(100) (simultaneously mounted on the same manipulator). Since calculations of either  $\mu_{\perp}$  or  $\mu_{\perp}$  can vary widely,  $^{1,23,28-32}$ the agreement between experiment and theory evident from Table II must be viewed as encouraging. It is interesting to speculate that as calculations of  $\mu_{+}$  become increasingly reliable, it may be possible to obtain accurate measurements of low-energy positron thermalization times using epitaxial systems such as Cu/W(110). This could be accomplished by measuring the diffusion length (as related to overlayer thickness) required to lose a "known" amount of energy  $(\Delta \mu_{+})$ , which would occur when the point  $E_3$  (Fig. 2) no longer shifts. Thermalization times are important in understanding the mechanism by which positrons lose energy, and present estimates range from less than 10 psec (Ref. 39) to on the order of 50 psec.40

Some of the most interesting data obtained over the course of these experiments were the result of excessive heat treatment of the Cu/W(110). This was the situation where we desorbed most but not all of the copper overlayer. An example of such a distribution [shown in Fig. 3(d)] reveals the "stepped" nature of the reemitted positron energy distribution that we interpret as evidence for three-dimensional islanding of the remaining copper. The continued high yield ( $\sim 25\%$ ) indicates that the islands are truly epitaxial, and the relative height of the steps provides a quantitative measure of the coverage. For the data which are shown in Figs. 3(d) and 4(d), the copper signal represents about 80% of the total height, which agrees very well with the AES result of 78%. The agreement between Auger peak amplitude and positron reemission data confirm that the islands are at least several monolayers thick.<sup>20</sup> In addition the present results indicate that the islands are likely isolated on a relatively clean tungsten substrate, as evidenced by the distinctive sharpness of the two contributions to the distribution shown in Fig. 3(d). As was mentioned previously, the low coverage of copper on tungsten is thought to cause inelastic loss processes which are responsible for the triangular distribution of reemitted positrons shown in Fig. 3(b).

The ability of this technique to be generally applied to the study of overlayer agglomeration depends, of course, on the system. It is necessary not only that  $\phi_+$  be negative for both substrate and overlayer, but also that the values be sufficiently different that the "stepped" structure evident in Fig. 3(d) [and 4(d)] be resolvable. If, however, these conditions are satisfied, it is obvious that islanding is

taken from Schulte in Ref. 1 and represent models presented by various authors (Refs. 29-31). The experimental results

TABLE II. This table contains theoretical estimates for positron and electron chemical potentials ( $\mu_{+}$  and  $\mu_{-}$ , respectively), and the resultant expected shift in the point  $E_3 [\Delta E_3 \equiv -(\Delta \mu_{+} + \Delta \mu_{-})]$  as defined in Fig. 2. Two values of  $\Delta E_3$  (theory) are shown because of the widely different methods for calculating  $\mu_{-}$ . All  $\mu_{-}$  values [(i) and (ii) in the table] were

are taken from Ref. 15 for Cr and Al, and Table I of this study for W and Cu.								
	Reference	<i>A</i> Cr(100)	<i>B</i> Al(100)	<i>A</i> W(110)	<i>B</i> Cu(111)			
$\overline{E_{\rm corr}}$ (eV)	28	- 10.2	-8.6	- 10.2	-9.3			
$E_{\rm corr}$ (eV)	32	- 9.48	-8.35		-9.23			
$E_0$ (eV)	32	+ 5.60	+ 4.41		+ 5.11			
$E_0$ (eV)	23	+ 6.3	+ 4.8	+ 6.3	+ 4.9			
$\mu_{+} (\equiv E_0 + E_{\rm corr})$	32	-3.88	- 3.94		-4.12			
$\mu_+$	28 and 23	-3.9	-3.8	-3.9	-4.4			
$\mu_+$	31	-3.5		-3.9	4.6			
Average $\mu_+$		-3.76	-3.87	-3.9	-4.37			
$\Delta \mu_+ [\equiv \mu_+(B) - \mu_+(A)]$		-0.11		-0.47				
μ	(i)	+ 1.20	-0.64	+ 1.24	-0.55			
$\mu_{-}$	(ii)	0		+ 1.53	-1.47			
$\Delta \mu_{-}[\equiv \mu_{-}(B) - \mu_{-}(A)$	(i)	-1.84		-1.79				
$\Delta \mu_{-}$	(ii)	-0.64		-3.00				
	(i)	+ 1.95 eV + 0.75 eV		+ 2.26 eV + 3.47 eV				
$-(\Delta \mu_+ + \Delta \mu)$ theory	(ii)							
$-(\Delta \mu_+ + \Delta \mu)$ experiment		+ 1.5		+ 2.64				

characterized in a straightforward manner using reemitted positrons. Indeed, what the technique lacks in versatility it makes up for in its ease of interpretation relative to the more conventional studies based on Auger electron spectroscopy.<sup>20,41</sup>

#### **V. CONCLUSIONS**

We have utilized a beam of variable-energy positrons to measure the positron work function, reemitted positron yield, and energy distribution for a W(110) crystal as a function of copper coverage. We find evidence that the interface between the copper and tungsten is sufficiently disordered to trap a considerable fraction of the thermalized positrons in open volume defects. The origin of the defects is uncertain, although it is suggested that they are the result of incomplete coverage of the tungsten substrate by the first (commensurate) monolayer of copper. The effect of positron localization is removed by annealing the Cu/W(110) system to about 1225 K. This temperature coincides with that required to desorb the first monolayer of copper on W(110) (Ref. 21) and is much higher than is needed to recover open-volume defects in the bulk copper overlayer.<sup>38</sup> These data couple with an anomalous dependence of the reemitted positron yield on incident energy [that was observed for the as-deposited Cu/W(110)] to provide strong evidence that the defects observed are associated with the interface and not with the bulk copper overlayer. The study of interfacial order is a field in which the unique open-volume defect affinity of the "slow" positron probe promises to make further contributions in the future. In addition the data offer a rare examination of theoretical calculations of positron and electron chemical potentials, yielding encouragingly close agreement.

After extensive annealing of the Cu/W(110) sample our results show clear evidence for the formation of three-dimensional copper islands on the W(110) substrate, such as were previously reported.<sup>19–21</sup> The reemitted positron energy distribution allows accurate quantification of the relative two-dimensional coverage of the surface by these islands.

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