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Temperature Dependence of the Work Function of Cu Layers on a W(110) Plane

Robert Gomer

The University of Chicago
The James Franck Institute
5640 South Ellis Ave., Chicago, IL 60637

Office of Naval Research
Physical Sciences Division
800 N. Quincy, Str., Arlington, VA 22217

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TEMPERATURE DEPENDENCE OF THE WORK FUNCTION OF Cu
LAYERS ON A W(110) PLANE

M. Chelvayohan and R. Gomer

Department of Chemistry and
The James Franck Institute
The University of Chicago
Chicago, Illinois 60637

ABSTRACT

Temperature coefficients of work function for Cu layers in the range 0 ≤ n ≤ 6 where n is the number of monolayers were measured from 90-500 K by a Kelvin probe method. dφ/dT is negative at all coverages and has a strong maximum of 6 × 10^-3 eV/K at n = 1 at 90 K. A qualitative discussion of these findings is given. The design and operating characteristics of the Kelvin probe are also described.

INTRODUCTION

In the course of following the thermal desorption of CO adsorbed on Cu layers on W(110), i.e. W(110)/Cu^x_n/CO by work function changes a substantial temperature coefficient of work function was noted for the substrates and investigated in some detail. We subsequently became aware of dφ/dT measurements by Kolaczkiewicz and Bauer [1] (KB). The measurements of these authors were mostly done at higher temperatures and overlap only very partially with ours. They also were obtained by a different method. Since the present measurements were carried out with a Kelvin probe of somewhat simpler design than similar probes described in the literature [2] we also include
a description of the probe.

**EXPERIMENTAL**

**General**

The main apparatus and the procedures for depositing Cu and determining its coverage on the W(110) substrate have been described in detail previously [3]. To recapitulate briefly, the Cu monolayer coverage was found from the break in the Auger intensity of the Cu LVV peak which coincided with the dose required to just not produce a second layer desorption peak in temperature programmed desorption. Submonolayer amounts were determined in terms of the dosing time relative to that required for a monolayer. In order to avoid depositing Cu on the vibrating electrode a shield was added to the Cu source which prevented the vibrator from receiving a Cu deposit, but still permitted normal dosing of the crystal and monitoring of the Cu source flux by the quadrupole mass spectrometer [3]. The absence of the Cu deposit on the vibrator could be established by running the Cu source, cleaning the crystal and demonstrating that no change in contact potential resulted.

**Kelvin Probe**

The probe was designed to be mounted on a 2-3/4" Conflat flange, entering the bell jar of the system from the side and ca. 10 cm below the plane in which the crystal rotates from and to various measuring devices, e.g. mass analyzer, Leed system, Auger, UPS, etc. It was considered desirable not to introduce a solenoid into the vacuum chamber and also to be able to float the probe electrode off ground. This was accomplished by the design sketched in Fig. 1. The principal elements are a 0.625" O.D. thin-walled stainless steel tube, TIG welded into the center of a 2-3/4" Conflat flange, and welded shut at its interior end. The solenoid, to be described later can be placed inside this tube or removed during bake-out and is thus exterior to the vacuum
A spring, formed from a strip of stainless steel 2-2.5mm wide and 0.02" thick, of total length 3/4" was bent into a right angle. To the longer side, (0.5") a small rectangular piece of μ-metal, 0.25" x 0.2" and 0.028" thick was spotwelded on the inside of the right angle, i.e. so that it would be closest to the end of the tube after final assembly. To the outside of the stainless steel strip a 0.02" diameter tungsten wire, bent as shown in Fig. 1 was spotwelded. The free end of this wire was connected to another length of 0.02" diameter W wire via a Nonex bead, kept as small as possible to reduce mass, so that the upper W wire was electrically insulated from the driver assembly. The horizontal portion of the stainless steel strip, ca. 0.25" in length was spotwelded to the 0.625" O.D. tube as shown. In order to keep the distance between the μ-metal platelet and the end of the stainless steel tube approximately 0.02" a suitable piece of shim was used as spacer during the welding of the assembly to the tube.

A piece of 0.01" Pt wire carrying the probe electrode was spotwelded to the upper end of the second 0.02" diameter W wire. The electrode consisted of a small piece, 2mm x 4mm of 70% transmission Mo Lektromesh whose back face, i.e. the side not confronting the sample, was spotwelded to the 0.01" Pt wire.

The signal take-off lead consisted of a 0.05" diameter tungsten rod running parallel to the main stainless steel tube over most of its length and then bent upward at its interior end. This rod was covered with Nonex over its entire length except for a 3mm portion at each end. Before sealing this rod into a 1/4" Kovar-Nonex press seal, TIG welded into the Conflat flange, it was conductivized with tin oxide over all but the section used for the seal and for a millimeter or so at the interior end. Before conductivizing a 0.003" diameter Pt wire was sealed into the Nonex coating. The free end of this Pt wire was spotwelded to a second W rod in the press seal. This arrangement permitted the electrical shielding of the takeoff lead to be floated off
ground; in fact, it was connected to the common point of the amplifier, to be described later. Without this precaution excessive pick-up was experienced. A 0.003" diameter Pt wire was also spotwelded to the upper of the two 0.020" diameter W wires, just above the Nonex bead, wrapped around this wire moderately tightly for two turns, wrapped similarly around the 0.05" W rod and then spot-welded to the latter. This was done to reduce fatigue and stress in the thin Pt wire and the spotwelds.

It was found important to make all bends in the vibrator assembly, i.e. in the 0.02" W wires as sharp as possible to avoid vibrational modes with large vertical rather than horizontal displacement of the electrode.

The solenoid assembly consisted of a soft iron cylinder, 1.5" long and 0.2" in diameter, wrapped with five layers of 80 turns each of #28 gauge copper wire. At its back end the Fe core was connected to a second Fe piece in the form of quarter cylinder (sliced lengthwise) and also 1.5" long, via a Fe cross piece. This served to confine and concentrate magnetic flux to the region near the solenoid pole faces thus greatly reducing (a) the current required to drive the vibrator and (b) pick-up caused by magnetic induction. In order to reduce the latter even more the solenoid was wrapped with six turns of Conetic AA sheet, 0.002" thick.

The solenoid was driven by an oscillator consisting of an ICL 8038 function generator chip, and a suitable power amplifier and produced a sinusoidal output from ~20 to 1000 Hz with drifts of < 0.1 Hz/hour. The vibrator could be driven at is fundamental or one of several overtones. The fundamental was ~80 Hz; overtones at ~200-400 Hz were normally used to reduce response time and increase sensitivity. The required solenoid current increases with frequency. Thus the chosen frequency depends somewhat on the time constant requirements. In most measurements a value of ~200 Hz for the actual vibrator
frequency was chosen requiring \( \approx 0.1 \) amperes of solenoid current and giving vibrational amplitudes of \( \approx 0.5 \) mm. Since the driver was \( \mu \)-metal the oscillator frequency was in each case half the vibrator frequency, which also helps to reduce pick-up. The signal from the vibrating electrode was fed into an AD 515 current to voltage converter using a \( 10^8 \) ohm feedback resistor. The output from the latter was fed into an HR-8 lock-in amplifier set via a frequency doubler to twice the oscillator frequency. In closed loop mode the output from the HR-8 was connected to the common point of the AD 515 amplifier, thus providing feedback and balancing the circuit. Reproducibility to \( < 0.001 \) volt was easily obtained, with very little long term drift. Response times were of the order of 100 milliseconds.

With the arrangement used here, namely electrical isolation of the take-off lead from the driving unit no detectable signal was seen (at the sensitivities used for actual measurements) when the crystal was rotated away from the vibrating electrode for potential differences up to \( \pm 3 \) volts between vibrating electrode and the bell jar of the vacuum system. Thus no compensating voltages are required and \( \Delta \phi \) measurements can be carried out with the vibrating electrode rather than the crystal off ground. When measurements were made with heating current from the temperature controller passing through the crystal, 2 precision 100 ohm resistors were placed between the potential leads of the crystal and their midpoint taken as that of the crystal center. The vibrating electrode was then tied to this point via the intervening balancing voltage developed by the HR-8 amplifier. In this arrangement the HR-8 was kept off ground by an isolation transformer and the inputs to the y axis of the recorder used to plot potential differences between crystal and vibrating electrode were also floated.
Measurement Procedure

Measurements were carried out by dosing Cu with the crystal at 300 K. Annealing of the Cu deposits at 900 K was carried out only for $\theta > 2$ monolayers, since it was found that no changes in $\Delta \phi$ resulted for smaller Cu deposits. The coolant reservoir was already filled with liquid $N_2$ during Cu deposition; the crystal was then allowed to cool to its base temperature, ~90 K before the first $\Delta \phi$ measurement. Changes in $\Delta \phi$ were then recorded when the crystal was heated to and kept at a given temperature. Reversing the crystal current did not affect the $\Delta \phi$ values obtained. It could also be shown that the observed changes did not result from RI drops in the crystal during heating: When the temperature controller was turned off the $\Delta \phi$ values decayed slowly in agreement with the cooling rates of the crystal, rather than instantaneously as would have been the case if RI drops played a role.

Finally thermal emfs must be considered. Since the Mo vibrating electrode remains at constant temperature, 300 K, and all connections between the W crystal and this electrode remain at constant temperatures, the only emf which needs to be considered is that of tungsten between 300 K (the temperature of the Mo electrode) and $T_X$, the temperature of the crystal. The absolute thermoelectric power of W is known [4]. Its mean value for $300 \leq T \leq 500$ K can be found from the data in Ref. 4 to be 4.25 microvolts/K, while that in the range $80 \leq T \leq 300$ K is -1.38 microvolts/K. Thus the contribution to $d\phi/dT$ is the order of $0.4-0.1 \times 10^{-5}$ eV/K and can be neglected, relative to the coefficients measured.

RESULTS AND DISCUSSION

Work function changes relative to clean W(110) as function of Cu coverage for annealed and unannealed layers all deposited at 300 K and measured at 90 K are shown in Fig. 2. These results are in good agreement with those
of KB. For instance, for 1 monolayer KB find $\Delta \phi = -725$ meV at 300 K while we obtain -680 meV at 90 K. If our results are corrected to 300 K they become -717 meV. Figure 3 shows $\Delta \phi$, measured from the 90 K values as function of temperature for various coverages; except for $T < 150$ K the curves are nearly linear. Figure 4 shows the corresponding $d\phi/dT$ values at ~90 K and near 450 K as function of coverage; $-d\phi/dT$ at 90 K is consistently higher than at 400 K. Also shown are the values obtained by KB near 400 K which extend only to 2 monolayers. The agreement between the two sets of data is very good where overlap exists except for $n = 0$ and $n = 2$. It should also be mentioned that KB's measurements start at 400 K and go up, while our start at 90 K and stop at 500 K, so that the overlap is only very partial.

$d\phi/dT$ for clean W(110) has been also measured by Swanson and Crouser [5] from the change in slope with temperature of field emission energy distributions, using a retarding rather than a dispersive energy analyzer. The value obtained was $-1.7 \times 10^{-4}$ eV/K, much higher than our value of $5.8 \times 10^{-5}$ eV/K, or BK's value $8 \times 10^{-6}$ eV/K. Swanson and Crouser, however, measured a value of $\phi(110) = 5.9$ eV at low temperature which is known to be too high by a factor of 1.12 [6]. That alone should not have caused the decrease in $\phi$ with $T$ to be so high, but the field emission method is subject to enhanced emission from isolated W atoms on the plane, which are likely to be generated by heating and which will give spuriously low values of $\phi$. It therefore seems reasonable to assume that the Swanson and Crouser values are too high. $d\phi/dT$
for Cu has also been measured by Blevis and Crowell, [7] who used a retarding field method in ultrahigh vacuum but failed to clean their surfaces except by heating in vacuo. Their value for Cu(111), relevant to thick layers measured in this work, is $-3.4 \times 10^{-4}$ eV/K; for Cu(100) they obtained an even higher value, $-13.8 \times 10^{-4}$ eV/K. Even their Cu(111) value is a factor of 6.8 higher than ours for 6 Cu layers on W(110). It seems very probable that this high value resulted from surface contamination, since it is now known that Cu cannot be cleaned by heating only. This is also suggested by the fact that Shelton [8] found much higher temperature coefficients of work function on a dirty than on a clean Ta(211) crystal.

The present results and those of KB are in close agreement where overlap occurs and we can therefore assume that they represent the behavior of Cu layers on W(110). Two facts stand out: $d\phi/dT$ is negative for all coverages, including zero, and $-d\phi/dT$ has a strong maximum at one monolayer. The decreases in $\phi$ with T for the clean surface has been explained by numerous workers on thermodynamic grounds: At the melting point $\phi$ must be equal for all planes so that $\phi$ must decrease with T for high work function planes like (110) [5]. Similarly, for very thick Cu layers which simulate Cu(111) i.e. a closepacked Cu plane, $\phi$ is also higher than on atomically rough planes and must decrease with T.

The increase in $-d\phi/dT$ for $0 \leq \theta \leq 1$ follows immediately if $(dP/dT)_W < (dP/dT)_Cu$ where $P$ is the dipole moment per surface atom of W or Cu respectively. If, in the temperature range of our experiments, Cu is either all in the form of non-interacting atoms or all in the form of islands, or if $dP/dT$ is independent of the state of aggregation, we can write

$$(d\phi/dT)_{obs} = (1-\theta)(d\phi/dT)_W + \theta(d\phi/dT)_Cu \tag{1}$$

where $\theta$ is fractional Cu coverage, and $(d\phi/dT)_W$ the temperature coefficient of
work function for a clean W surface and \((d\phi/dT)_Cu\) that for a surface covered with a monolayer of Cu. Thus \(\theta(d\phi/dT)_Cu\), the change resulting from Cu adsorption, should be linear in \(\theta\). Figure 5 shows this to be the case, within experimental error. The \(d\phi/dT\) data of KB at very high temperature where Cu forms a 2-dimensional gas give much higher values than those obtained at the temperature of the present experiments and it therefore seems probable that we are dealing mostly with Cu islands.

A maximum in \(-d\phi/dT\) must follow if \(-d\phi/dT\) for thick layers is less than for a monolayer (which is the case) but this does not explain why the maximum occurs at \(\theta = 1\) or why \(-(d\phi/dT)_{Cu \, bulk} < -(d\phi/dT)_{\theta = 1}\). We consider first the behavior at \(\theta < 1\). As just pointed out \(dP/dT\) is essentially constant in this regime so that we need only consider results at \(\theta = 1\). The first possibility for explaining a negative value of \(d\phi/dT\) is simply some roughening of the layer by heating. It has been known since the work of Smoluchowski in 1941 [9] that \(\phi\) decreases with surface roughness because of electron spill-over which makes exposed metal atoms more positive, thus providing a surface dipole with positive end outward. Since we are probably dealing with islands at all \(\theta \leq 1\) this effect could occur even at low \(\theta\). It is conceivable that the effect could be much larger for a monolayer of Cu on W(110) than for (essentially) bulk Cu(111) since the epitaxial Cu monolayer is more loosely packed than the closepacked Cu(111) surface.

At least formally we can also consider the problem in terms of the average of \(dP/dT\). We have at \(\theta = 1\)

\[
\Delta \phi = 4\pi Pc
\]  
(2)

where \(c = 1.4 \times 10^{15}\) is the number of Cu atoms/cm\(^2\) and \(P\) the dipole moment per ad-atom. Thus

\[
\left(\frac{d\phi}{dT}\right)_{\theta = 1} = \frac{d\Delta \phi}{dT} = -4\pi \times 300 \, c(dP/dT) \, eV/°K
\]  
(3)
where

$$P = q \cdot x$$  \hspace{1cm} (4)$$

is the dipole moment per Cu atom and \(q\) is charge in e.s.u. and \(x\) dipole length in cm, and

$$\frac{dP}{dT} = \frac{d(q \cdot x)}{dT} = \frac{dx}{dT} [q_o + x \frac{dq}{dx}]$$

$$= \alpha [P_o + x^2 \frac{dq}{dx}]$$  \hspace{1cm} (5)$$

where \(\alpha = (dx/dT)/x\), the linear expansion coefficient, and subscripts refer to equilibrium values. Combining Eq. (4) with Eq. (1) we can also write

$$\frac{d\Delta \phi}{dT} = \alpha(\Delta \phi_o + x \frac{d\Delta \phi}{dx})$$  \hspace{1cm} (6)$$

For 1 monolayer \(\Delta \phi \approx 0.7\) eV. The expansion coefficient of a monolayer of Cu on W(110) is not known but is unlikely to be an order of magnitude greater than that of bulk Cu, in particular since the W-Cu bond is stronger than the Cu-Cu in bulk copper, as indicated by Bauer's thermal desorption work [10]. Thus a safe upper limit would be the bulk Cu value \(\alpha_{Cu} = 1.7 \times 10^{-5} \text{ K}^{-1}\).

On this basis the first term in Eq. (5) contributes negligibly to \(d\Delta \phi/dT\), and the observed value results from \(x^2 \frac{dq}{dx}\). If \(x_o \approx 2\) Å \(dq/dx \approx 0.1\) e/Å, where e is the positron charge (i.e. positive charge in units of electron charge).

This value is quite high, but even more interesting is the fact that the charge deficiency on Cu increases with distance from the W surface. If Cu were removed to infinity, i.e. beyond the range of the chemisorption interaction the charge deficiency would have to vanish, since the ground state is \(W^0_{\text{solid}} + Cu^0\). This follows from the fact that \(I_{Cu} = 7.7\) eV while \(\phi\) for the Cu covered surface is 5.3-0.7 = 4.6 eV so that \(I - \phi = 3.1\) eV meaning that formation of \(W^-_{\text{solid}} + Cu^+\) from \(W^0_{\text{solid}} + Cu^0\) is endoenergetic by 3.1 eV when Cu is far from the surface.

As already noted the sign of \(dq/dx\) can be explained in terms of surface roughening. It is also possible, in a crude way, to rationalize the effect
in terms of the Newns-Anderson model of chemisorption [11] which concerns itself with single ad-atoms and ignores, at least in its simpler versions, adsorbate-adsorbate interactions. For an adsorbate like Cu whose bonding level, i.e. 4s lies at 7.7 eV below vacuum i.e. in the filled portion of the W conduction band the picture depicted in Fig. 6 gives a qualitative explanation of the electron population on Cu. At large distance the adsorbate level is discrete and at 7.7 eV below vacuum. As x decreases the level is shifted upward by an image potential and also broadened by interaction with the substrate. In the simplest case the resulting local density of states would be Lorentzian with a half width 1/\Delta, and would be shifted downward in energy by A, A being the Hilbert transform of \Delta[11]. In general both A and \Delta are functions of energy. The electron deficiency on the Cu atom is then described by the portion of the LDOS above the Fermi level. As x increases from the equilibrium bond distance several things will happen: (1) the resonance is shifted downward in energy as the image potential decreases; (2) It narrows as the hopping integral which enters into \Delta decreases; (3) it shifts upward as A decreases. The first two effects increase the electron population on Cu, the third decreases it. It should also be noted that the energy dependence of A and \Delta makes it likely that the shape of the resonance changes in such a way as to contract it more at lower than at higher energies as x increases. This would also give the unfilled portion greater relative weight, i.e. increase the positive charge on Cu as x increases slightly from its equilibrium value. It is therefore possible that over a small range of x \text{d}q/\text{d}x is positive as observed. As already pointed out eventually its sign must reverse as the resonance shrinks back to a discrete level below E_F.

It should be pointed out that the two rationalizations given here are not inherently different but simply stress different aspects of the actual situation. If either model were pursued self-consistently, taking account of lateral interactions in the Newns-Anderson case, they should give the same results.
Why is dP/dT much smaller for θ > 1? The answer is probably easier to see in terms of the Newns-Anderson model, on the basis of the rather different hopping integrals involved, which change A and Δ. For 2 layers the effect of underlying W is still felt and now apparently leads to a much smaller dq/dx. As the layer thickness increases the bulk Cu(111) value is reached essentially at n=3.

It need not be stressed that the above cannot take the place of real calculations and is only an attempt to justify the observations by very qualitative arguments. However, these describe an interesting physical situation.

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REFERENCES

FIGURE CAPTIONS

1) Schematic diagram of Kelvin probe assembly. For simplicity of presentation the press seal carrying the signal take off lead has been drawn as if vertically above the stainless steel tube. In order to bring the assembly through a narrow port the take off lead is in fact to one side of the main tube.

2) $\Delta \phi$ relative to clean W(110) vs. dosing time. All depositions were carried out with the crystal at 300 K and measurements were made at 90 K. (□) unannealed, (○) annealed at 850 K. Solid circles and squares are annealed and unannealed results from Ref. 1.

3) $\Delta \phi$ relative to the 90 K values as function of temperature for different layer thicknesses, marked in units of monolayers, n, on the figure. The curves have been displaced from each other by 10 meV for ease of viewing.

4) $-d\phi/dT$ vs. layer thickness. (○) values near 90 K; (x) values near 500 K; (Δ) values near 400 K from Ref. 1.

5) $\Theta (d\phi/dT)_Cu$ vs. relative coverage $\Theta$ for $0 \leq \Theta \leq 1$. $-(d\phi/dT)_Cu$ refers here to the change due to Cu when $\Theta = 1$.

6) Schematic diagram illustrating a possible mechanism for explaining positive dq/dx for an adsorbate like Cu. M metal, A adsorbate. $E_F$ Fermi level. The sharp adsorbate level $\varepsilon_a$ broadens into a resonance of width $2\Delta$, which is filled to $E_F$, the empty portion corresponding to the electron deficiency on A. The center on the resonance is roughly given by $\varepsilon_a + \Lambda - V_{im}$ where $\Lambda$ is a negative quantity and $V_{im} \approx e^2/4x$. $\Lambda$ is shown at the equilibrium distance, at large x, and at an intermediate distance where x dependences of $\Lambda$, $\Delta$ and $V_{im}$ result in a slight increase in the empty portion of the resonance. Distances are not drawn to scale.
$\Delta \phi$ meV

Dosing Time, sec

W(110)/Cu

- unannealed
- annealed at 850 K

$\theta = 1$
Fig. 3

$-\theta (d\phi/dT)_\text{Cu} \text{ meV/°K}$

$\theta$

0.2 0.4 0.6 0.8 1.0

0 2 4 6 8 10 12 14 16
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