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THE DEPENDENCE OF WORK FUNCTION ON THICKNESS IN EPITAXIAL Cu-Pd SYSTEMS

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Abstract

Changes in work function have been measured with a Kelvin probe for the initial stages of epitaxial growth of (111) Cu on (111) Pd and (111) Pd on (111) Cu and for CO adsorption on selected bilayers at room temperature. The results of this study show that, at low metal coverages, the overlayers have properties which differ significantly from those of bulk crystals. One of the most interesting observations was that a quarter monolayer of Cu on Pd(111) increases the saturation work function change upon CO adsorption by more than a factor of three as compared to a thick Pd(111) film.

Introduction

The modification of metal surfaces plays an important role in the fields of catalysis and thermionic emission. This study was concerned with the alteration of the chemical and electronic properties of metal surfaces by the adsorption of atoms of a different metal. Specifically, the Pd-Cu system was investigated using work function techniques. The work function, defined as the minimum energy required to remove an electron from the surface of a metal, is an important parameter for investigating changes in the electronic structure of a metal. It gives a direct and very sensitive indication of surface electronic structure changes as sub-monolayer deposits of a different metal are adsorbed. Similar investigations have been carried out on other bimetallic systems such as Cu/Pt(111) [7,16] and Pd on various refractory metal surfaces [8,10-12] but there are relatively few reports on the Pd/Cu system. Angle-resolved photoemission studies by Smith et al. for Pd on Cu(100) [13] and Pessa and Jylha for Pd on Cu(111) [9] have been carried out. The epitaxial growth and microstructure of Pd/Cu(111) bilayers have also been studied by a variety of techniques [3,4]. In addition, Asonen et al. have investigated Cu on Pd(100) [1] by low energy electron diffraction (LEED), Auger electron spectroscopy (AES), and angle-resolved ultraviolet photoemission spectroscopy.

In this paper, the effect of epitaxial sub-monolayer and thicker deposits of Pd on Cu(111) and Cu on Pd(111) were studied by measuring the work function change ($\Delta\phi$) as a function of overlayer thickness. Also, $\Delta\phi$ was measured during CO exposure to determine the effect that the overlayer had on the adsorption properties of the substrate metal. This work provides additional insight on the growth and electronic structure of metallic overlayers on dissimilar metal substrates.

Key Words: Palladium, Copper, Epitaxy, Thin Films, Work Function.

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Experimental

All of the experiments were carried out in an ion and titanium sublimation pumped stainless steel ultra-high vacuum chamber

capable of achieving a base pressure of 5×10^{-9} torr. The system contained two evaporation sources that were equipped with moveable shutters in order to have better control over the deposition of the overgrowth. The substrate films were deposited on air-cleaved mica, which was held at 150°C during deposition. Typically, the films were deposited at a base pressure of 9×10^{-9} torr, with the pressure rising to 2×10^{-8} torr during evaporation. These deposition conditions led to flat, well oriented (111) single crystal films, as determined by subsequent reflection high energy electron diffraction measurements. The Cu(111) substrate films were typically 300 nm thick and the Pd(111) films were 150 nm thick. The overlayers were deposited at room temperature with the thickness being measured in-situ with a quartz crystal. The precision in a given thickness measurement is estimated to be ± 0.01 nm. The overgrowth was deposited in quarter monolayer increments and the work function was measured between depositions. One monolayer (ML) of (111) Pd corresponds to 0.225 nm, as calculated from the lattice parameter. For (111) Cu, this value is 0.209 nm.

The work function measurements were made using a Kelvin probe apparatus. The probe measures the change in the contact potential difference (CPD) between the sample and a gold coated reference electrode as the surface of the sample is changed. This method is well documented in the literature and need not be discussed here [5]. The $\Delta\phi$ measurements could not be made simultaneously with adatom deposition because the probe must be shielded from the evaporation source. Therefore, after a reference CPD reading was recorded, the substrate was moved away from the probe and the desired thickness of overgrowth was deposited. The sample was then moved back to its original position and the work function change, as compared to the reference value, was measured. Both Cu and Pd overlayers were deposited in this way on their corresponding substrates up to a coverage of 1.0 nm. As a check on the accuracy of the sample manipulators, $\Delta\phi$ was measured several times upon moving the sample away from its reference position and back again. The average change was ± 10 meV.

After 1.0 nm of overlayer was deposited, the bilayer films were exposed to 1×10^{-6} torr CO, with $\Delta\phi$ being measured simultaneously. During CO exposure the gate valve to the ion pumps was partially closed to reduce the load on the pumps. After each CO exposure, the sample was heated rapidly to 200°C in order to desorb the CO adsorbate. The samples were then cooled to room temperature before subsequent experiments were carried out.

Results

Pd on Cu(111)

The work function change as a function of Pd thickness on a thick Cu(111) film is given in figure 1. The results shown are the average

values from three separate runs of the experiment. The individual runs all showed the same trends as the submitted plot, with an average deviation of ± 40 meV. The work function initially decreased to a value of -250 meV at an approximate coverage of 0.6 ML, followed by a near linear increase to a saturation value of +660 meV at a coverage of 3.0 ML. The work function remained essentially constant upon additional Pd deposition. These values were all measured relative to Cu(111). The work functions of bulk Pd(111) and Cu(111) are 5.60 eV and 4.94 eV, respectively [15]. Thus, the average saturation value of $\Delta\phi$ agrees well with the difference between the bulk single crystal values.

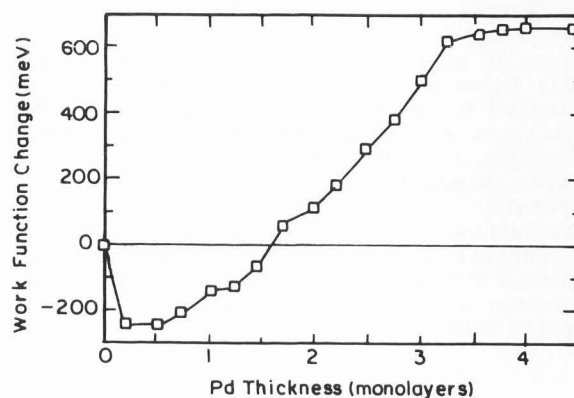


Figure 1. Change in work function with Pd overlayer thickness on 300 nm Cu(111).

In figure 2 the work function change is plotted as a function of CO exposure time for a thick Pd(111) film, a 1.0 nm Pd/Cu(111) bilayer, and the original Cu(111) substrate. The shapes of the first two curves are similar, but the bilayer has a saturation value of +735 meV, as compared to +600 meV for the thick Pd. The data for Cu(111) illustrates the well known fact that CO does not adsorb on Cu at room temperature under high vacuum conditions. An explanation concerning the long exposure is necessary since it is known that the CO saturation exposure on Pd(111) is less than 20 langmuirs [2]. The discrepancy is due to the method of $\Delta\phi$ measurement. The vibrating reed of the Kelvin Probe is separated from the sample by a distance of less than 1 mm. It therefore blocks gas molecules that are directed at the bilayer surface from the top; the gas molecules can reach the sample surface only from the sides. Thus, the actual CO pressure in the vicinity of the reed is much lower than the chamber pressure. This explanation qualitatively accounts for the observed long saturation times.

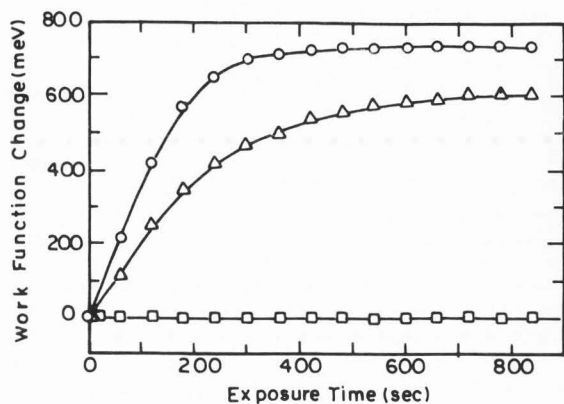


Figure 2. Change in work function with CO exposure time for 1 nm Pd/Cu(111) (O), Pd(111) (Δ), and Cu(111) (\square). (CO pressure = 1×10^{-6} torr).

Cu on Pd(111)

The average values taken from three separate experiments of the work function change as a function of Cu thickness on a thick Pd(111) substrate are shown in figure 3. In this case, the average deviation was ± 25 meV. The work function change decreased smoothly to a minimum value of -725 meV at a Cu coverage of 2.0 ML, followed by a small increase to a saturation value of -690 meV at a coverage slightly less than 2.5 ML.

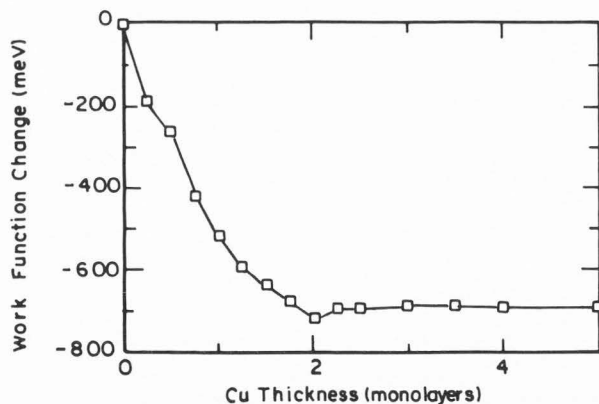


Figure 3. Change in work function with Cu overlayer thickness on 150 nm Pd(111).

The work function change on CO adsorption on the 1.0 nm Cu/Pd(111) bilayer is negligible compared to that for Pd(111). This result is consistent with the data in figure 2 where it was shown that Cu does not adsorb CO at room temperature. Thus, again, the overlayer behaves like a thick film when it is 1.0 nm thick.

However, this is not the case for smaller Cu coverages. For example, figure 4 also shows the CO exposure curve for a 0.05 nm Cu/Pd(111) bilayer as compared to a thick Pd(111) film and a 1.0 nm Cu/Pd(111) bilayer. The small Cu coverage of 0.05 nm actually increases the work function change upon CO adsorption by more than a factor of three, i.e., from 600 meV for pure Pd to 1940 meV.

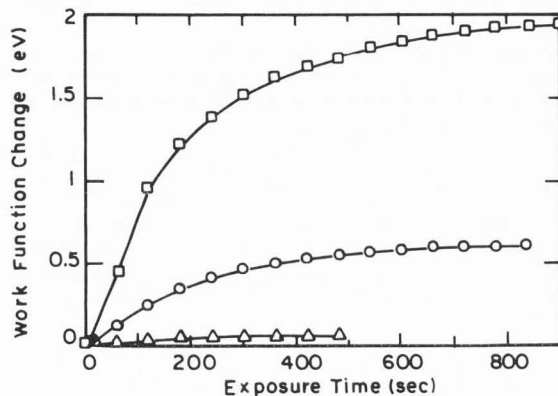


Figure 4. Change in work function with CO exposure time for 0.05 nm Cu/Pd(111) (\square), Pd(111) (O), and 1 nm Cu/Pd(111) (Δ). (CO pressure = 1×10^{-6} torr).

Discussion

Pd on Cu(111) Growth

For the purpose of this study, only the qualitative aspects of the curves will be discussed. Perhaps the most interesting feature of figure 1 is the initial decrease in $\Delta\phi$ as Pd is deposited up to an approximate coverage of 0.5 ML. Based on the bulk work function values of Cu and Pd, one would expect that adsorption of Pd on the Cu surface would cause an increase in the work function. This behavior is not totally unexpected, however, since Schlenk and Bauer found similar results for Pd on W(110) [12]. The reason for the decrease is believed to be due to the fact that there are two main factors that affect the work function. First, there is an electronic effect which is due to the difference in the electronic properties between the adatom and the substrate that results in charge transfer either from or to the substrate. Second, the work function is affected by the morphology of the surface, as discussed by Smoluchowski [14]. The Smoluchowski effect predicts that the work function of a surface will decrease as the surface is roughened. The physics of this phenomenon is well documented in the literature, and will not be discussed in any greater detail in this paper [14]. A combination of these two factors must be considered in the interpretation of the observed work function variation.

While roughening certainly occurs as the first Pd atoms adsorb on the Cu(111) surface, the electronic properties that are characteristic of the Pd adatoms are altered also. Angle-resolved photoemission studies of this system show that the characteristic Pd peak is small and shifted at coverages of less than 1 ML. It is not until a coverage of 0.7 ML that a distinct Pd peak begins to form and not until 2.3 ML that the bulk Pd electronic characteristics are established [9]. This result demonstrates that the Pd adatoms lose their characteristic identity in this low coverage range. Thus both roughening and the electronic interaction between the substrate and the adatoms are important.

Subsequent to the initial work function decrease, the near linear rise that follows suggests a Frank-van der Merwe layer by layer growth mode, which is in agreement with previous AES studies [4]. The tendencies for slight changes in the slope near the monolayer completion region may be due to the Smoluchowski effect [14]. During monolayer growth, the step density varies periodically, reaching a minimum when a complete monolayer is formed. At this stage, the surface is flattest. When more atoms are added to this smooth surface, the film roughens and the work function decreases. These periodic oscillations seem to be important only in the coverage range of 0.6-3.0 ML. Further depositions do not lead to further oscillations of the type that are seen in this intermediate region. Apparently, at 3.0 ML, the electronic character of the Pd is fully established and the roughening effect is no longer as important. These results suggest that the roughness effect is important only at coverages where the effects of the Cu substrate can still be felt by the Pd adatoms.

The CO adsorption experiments give further evidence that the bilayer has developed strong Pd characteristics at a 4.0 ML coverage. The similar Pd(111) and 1.0 nm Pd/Cu(111) exposure curves of figure 2 show that the bilayer behaves as a thick Pd film with respect to its adsorption properties. The increased saturation value for the bilayer may be due to the fact that the bilayer is not as smooth as a thick Pd(111) film. Also, the underlying Cu may still have an effect on the adsorption but more work must be done in this area to make any definite conclusions.

Cu on Pd(111) Growth

In this case, the roughness and electronic effects are more difficult to separate because they both cause the work function to decrease. The first 0.05 nm of Cu deposition results in the largest work function decrease for any single deposition. This first deposition on the flat Pd(111) surface is likely to lead to roughening because at this low coverage there is not enough Cu present to form a flat, continuous layer. The -200 meV change at 0.05 nm corresponds well to the decrease seen in the initial part of the Pd/Cu(111) curve. If the same arguments can be applied to this case, it is reasonable to assume that this portion of

the curve could be due largely to a similar roughening effect.

After the first deposition, the work function decreased to its minimum value as more Cu was deposited. The small dip in the curve that occurred at 1.75 ML may also be caused by roughness effects because at this coverage the Cu character of the overlayer is not yet well established. It is a real effect, having appeared in all three curves that were averaged to form the one illustrated in figure 3. With further deposition the 2nd ML is completed, the step density decreases and the film flattens, thus causing an increase in the work function. After 2.5 ML was deposited, there was very little variation in the work function upon further deposition. This result is similar to the Pd/Cu(111) case in that there are no oscillations after the Cu electronic characteristics have been established.

The 1.0 nm Cu/Pd(111) bilayer does not adsorb CO appreciably at room temperature as determined by a negligible work function change on CO exposure. The CO exposure curve for the 0.05 nm Cu/Pd(111) film supports the proposition that Cu adatoms are altered electronically upon adsorption. The enhanced work function change indicates that the bilayer acts as a unique material with properties that are different from either of its constituent atoms. This result is similar to that of Cu on Ru(0001), where the CO adsorption properties of a 1 ML bilayer are unlike that of either bulk Cu or Ru(0001) [6].

Conclusions

The variation in work function as a function of overlayer growth has been measured in order to learn more about the growth characteristics and stability of metals on dissimilar metal thin film substrates. The results of this study show that low coverages of metal adatoms may cause a strong alteration in the electronic structure of the surface. This alteration is best exemplified by the enhanced work function change on CO adsorption of the 0.05 nm Cu/Pd(111) bilayer as compared to Pd(111). Also, the work function of Cu(111) can be reduced by a 0.05 nm deposition of Pd, even though Pd has a higher work function. The specifics of the electronic interaction at low coverages are not well understood, but it is clear that the bilayer has properties different from both Cu and Pd in this low adatom coverage region. After 3.0 ML of overlayer has been deposited, the bilayers are shown to behave as if the overlayer were a thick film.

Acknowledgements

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Discussion with Reviewers

Reviewer 1: The working pressures in your experimental apparatus are very high (up to 2×10^{-8} torr) by ultra high vacuum surface science standards. What is the composition of the experimental vacuum gases?

Authors: After bakeout, the residual gas spectrum was typically 9% H₂, 58% He, 6% H₂O, 10% CO, 6% CO₂. The He arose from the ion pumps which pumped it when the experimental setup was being assembled and leak checked, Helium was subsequently re-emitted by the Ti films in the pump.

Reviewer 1: Although Cu is not very reactive one must admit that Pd is quite susceptible to H₂, CO, O₂, H₂O... adsorption. For example, Conrad et al, in Surf. Sci. 65, 245 (1977) give an O₂ sticking probability of 0.30 for Pd(111). How can you in the admittedly limited vacuum of your experiment claim that such effects as the submonolayer decrease in work function (found in Fig. 1) are solely due to roughness/electronic effects? What was the exposure (in Langmuirs) between film deposition and work function measurement?

Authors: Drift measurements for the probe exposed to the residual gas atmosphere were run repeatedly over the course of the experiments. That drift never exceeded 0.5 meV per minute and was therefore well within the precision of the measurements as stated in the text. (For CO adsorption, this drift represents the adsorption of 0.0008 monolayers/min.) Thus the possible effects of the residual gas background can be neglected.

Reviewer 1: You state that unusually long exposures were needed to reach a CO saturated state on Pd due to the shadowing of the vibrating reed. Is such an increase from 20 to ~800L (a factor of 40) consistent with what appears to be a needle encompassing a small solid angle as seen from the crystal? Might not the Pd be poisoned with the above impurity gases?

Authors: Approximate calculations indicated that the exposures would require at least two orders of magnitude longer times for a given partial pressure in the system in order to achieve the same saturation exposure that one would get if the Kelvin probe were not present. The results indicated in 2. above show conclusively that the Pd surfaces were not poisoned by the impurity gases.

Reviewer 1: It is known that Ag and Au will segregate on the surface of a Pd substrate; see J.C. Hamilton, Phys. Rev. Lett. 42, 989 (1979). Due to its position in the Periodic Table one would also anticipate that Cu would behave similarly. Because Cu may have a tendency to move to the vacuum/solid interface, have you thought of invoking Pd surface penetration to explain the initial work function decrease observed in Fig. 1? Previously published work by De Cooman et al., Surf. Sci. 128, 128 (1983), is

quite interesting in this respect. In their work on Pd-on-Cu films the Cu LEED features are reported to disappear after 2.5 Å (~one monolayer) deposition. One would think that the layer-by-layer growth mode proposed by De Cooman et al. would give sharp diffraction features at that coverage. Might not this diffraction behavior suggest an initially more reactive deposition process for Pd on Cu?

Author: The initial decrease in work function illustrated in Fig. 1 is not uncommon in the literature. It has been reported for (100)Pd/(100) Ag, (111)Pd/(110)W and (111)Pd/(110)Nb. Whether some interdiffusion of Cu and Pd occurs during deposition at room temperature is unknown. It certainly occurs during annealing at higher temperatures, as we will be reporting elsewhere. We also know that heating Pd-Cu bilayers to 225 C for 1 min. does not change the room temperature work function and thus suggests that no interdiffusion occurs at room temperature. With regard to the LEED work of De Cooman et al., it is not known why the LEED pattern disappeared at a thickness of 2.5 Å and then reappeared after 14.5 Å Pd had been deposited. Fujinaga (Surf. Sci. 84 (1979) 1) saw a similar effect at thicker Pd overgrowths on bulk Cu crystals. Clearly more work needs to be done to understand this phenomenon.