

Coverage and structure of ultrathin Pd films on Cu(100)

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The deposition of Pd on Cu(100) at 300 K was studied by low-energy electron diffraction (LEED), Auger-electron spectroscopy, and Rutherford-backscattering spectrometry. A clear maximum in the $c(2\times 2)$ LEED pattern intensity occurred at a Pd coverage of 0.55 ± 0.05 monolayers (ML), consistent with the surface-alloy model for this system. Breakpoints in the Auger intensity versus deposition-time curves were seen at 0.47 ± 0.05 and 0.93 ± 0.11 ML. A $p(2\times 2)$ LEED pattern was observed near 1-ML Pd coverage.

INTRODUCTION

The study of metal-on-metal overlayer systems provides both insight into the physics of crystal growth and the potential for novel overlayer structural, magnetic, and chemical properties.¹⁻³ Although in most cases an ordered overlayer is formed,^{1,4} surface-alloy formation has been observed for some systems, such as Au on Cu(100).^{5,6} The deposition of Pd on Cu(100) at 300 K has been studied by several authors.⁷⁻¹⁰ When a Cu(100) crystal is exposed to Pd at room temperature, a $c(2\times 2)$ low-energy electron diffraction (LEED) pattern is observed at low coverage. With increasing coverage the half-order spots reach a maximum in intensity and then fade out, leaving a diffuse (1×1) LEED pattern. It is believed that the maximum intensity of the $c(2\times 2)$ LEED pattern corresponds to the formation of an ordered 1:1 surface alloy of Pd and Cu, analogous to the (100) surface of Cu_3Pd (α'').^{11,12}

The Pd coverage associated with the maximum $c(2\times 2)$ LEED pattern intensity is still not known with certainty. Graham⁷ calibrated his Pd evaporator using the established work-function change for the deposition of Pd on W(110) and found the Pd coverage associated with this structure to be 0.8 monolayer (ML). Wu *et al.*¹⁰ have subsequently concluded that a coverage near 0.5 ML would be more consistent with their LEED IV measurements. In both cases the best $c(2\times 2)$ LEED pattern was observed just before the first change in slope (breakpoint) in the Pd Auger intensity versus deposition time curve. The Pd exposure corresponding to the best $c(2\times 2)$ pattern was determined visually in these studies, and no direct coverage measurements were made.

In this paper we present the results of our study of the deposition of Pd on Cu(100) at 300 K. Auger-electron spectroscopy (AES) and LEED measurements are correlated with Rutherford-backscattering spectrometry (RBS) measurements to provide structural information and absolute Pd coverages.

EXPERIMENTAL DETAILS

The experiments were done in a UHV chamber equipped with four-grid LEED optics for LEED and Auger measurements, quadrupole mass spectrometer, sputter ion gun, Pd evaporation source, and bakeable surface barrier detectors for RBS measurements. The chamber has a base pressure below 10^{-10} Torr and is interfaced to a 2.5-MV Van de Graaff accelerator via a differential pumping bench.

The Cu sample was a single crystal cut and polished to expose the (100) face. The crystal surface was cleaned by argon-ion sputtering (2 keV, $2\ \mu\text{A cm}^{-2}$) at room temperature followed by annealing in vacuum at 700 K. Surface cleanliness was confirmed by AES. Pd was deposited onto the surface from a sublimation source consisting of a Pd wire heated by electron bombardment.

The LEED measurements were made with a video LEED system of our own design which consists of a silicon-intensified (SIT) video camera and Beta video cassette recorder interfaced to an IBM AT computer via image processing boards. The image processing software calculates the background intensity for each measurement and subtracts it to give the true spot intensity.

AES spectra were taken at 2.5-keV incident beam energy with 10-V peak-to-peak modulation at 1 kHz on the retarding grids. The clean crystal spectra displayed the diffraction peaks below 300 eV first studied by McDonnell, Powell, and Woodruff.¹³

The Pd coverages were determined by RBS. An incident beam of 2.0-MeV $^4\text{He}^+$ was used to ensure separation of the Pd and Cu backscattering peaks. The backscattered ions were detected by a surface barrier detector at 118° scattering angle. The beam dose was measured on a transmission Faraday cup with a 25% duty cycle. The Pd backscattering yield was converted to an absolute Pd coverage through comparison with the Bi backscattering yield from a Bi implanted Si standard. The Bi content of the standard is known with 2% precision.

The clean crystal was exposed to Pd from the evapora-

tion source in small increments and the LEED, AES, or RBS measurement made between exposures. In the Auger experiments, the peak-to-peak amplitudes of the Cu (920 eV) and Pd (330 eV) derivative Auger spectra were measured. The peak-to-peak amplitude measured at 330 eV originates from both the 326- and 330-eV Pd Auger transitions. The amplitudes of these spectra will be referred to as the Cu and Pd Auger intensities. No impurities were detectable by AES even after an experiment of several hours duration. The crystal temperature remained between 298 and 302 K at all times.

RESULTS

Figure 1 shows the Pd Auger intensity and the Pd/Cu intensity ratio as a function of deposition time. There is a marked change in slope (breakpoint) in both lines between 5 and 5.5 min deposition time. The inset to Fig. 1 extends the Pd Auger intensity data to higher exposures and shows a second breakpoint near twice the deposition time of the first. The second breakpoint was seen in all experiments, but was more apparent in the Pd Auger intensity plots than in the Pd/Cu intensity ratio plots. The Auger breakpoints occurred at the same Pd/Cu Auger ratio regardless of the rate of deposition. The first breakpoint corresponds to a ratio of 1.83 ± 0.08 and the second to a ratio of 3.5 ± 0.15 . The Pd/Cu Auger ratio corresponding to the maximum intensity in the $c(2 \times 2)$ LEED pattern was also independent of deposition rate, indicating a unique correspondence between Auger ratio and coverage.

In our experimental geometry, light from the evaporation source interfered with the surface barrier detector used in the RBS measurements. For this reason, the evaporator had to be shut off during RBS measurements,

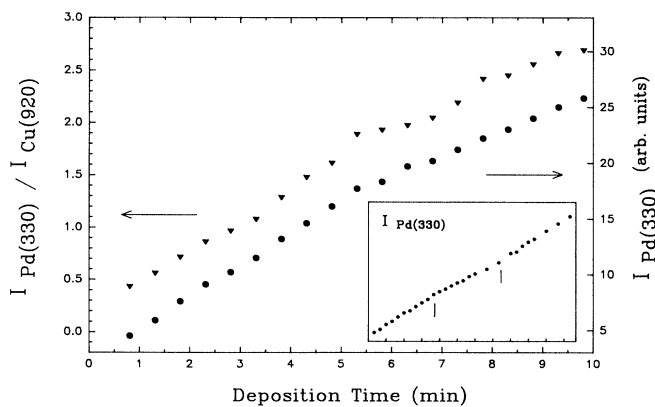


FIG. 1. Pd peak-to-peak Auger amplitude measured at 330 eV (right scale) and ratio of the Pd to Cu (920 eV) Auger peaks (left scale) as functions of Pd deposition time. The inset extends the Pd Auger amplitude to higher Pd deposition times. The vertical bars give the approximate locations of the breakpoints.

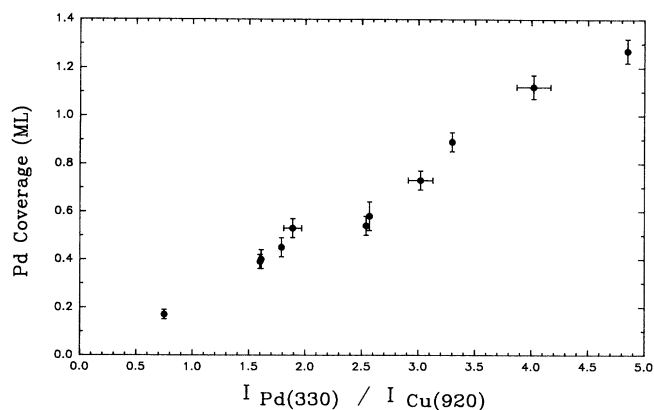


FIG. 2. Pd coverage as a function of Pd to Cu Auger intensity ratio.

making the deposition time scale much less precise for the RBS measurements than it was for the Auger intensity versus deposition time curves discussed above. Since the Pd/Cu Auger ratio was uniquely related to coverage, the Pd coverage was measured by RBS as a function of Pd/Cu Auger ratio rather than deposition time (Fig. 2). The horizontal error bars give the uncertainty in the Auger ratio determination and the vertical error bars give the statistical error in the RBS measurements. Since the Pd coverage is proportional to the deposition time, the data of Fig. 2 should form straight line segments as observed in the Pd/Cu Auger ratio curve of Fig. 1. The precision of the RBS data was insufficient to allow these segments to be drawn on the figure. We find the Pd coverage to be 0.47 ± 0.05 ML at the first Auger breakpoint and 0.93 ± 0.10 ML at the second.

The intensities of the $(\frac{1}{2}, \frac{1}{2})$ LEED spots at 123 eV were measured as a function of Pd/Cu Auger ratio. The Pd/Cu ratio values were converted to coverages using the data of Fig. 2, and the $c(2 \times 2)$ intensity replotted as a function of coverage in Fig. 3. Our LEED observations are in qualitative agreement with those of Wu *et al.*¹⁰

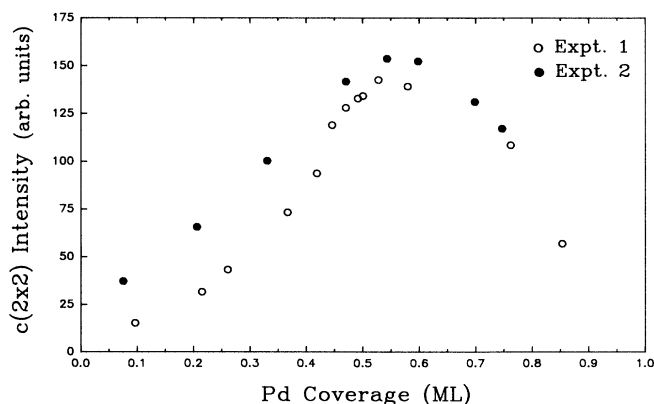


FIG. 3. Intensity of the $(\frac{1}{2}, \frac{1}{2})$ LEED spots as a function of Pd coverage for two separate experiments.

and Graham.⁷ The $c(2 \times 2)$ pattern is first observed visually near one quarter monolayer, although the increase in $(\frac{1}{2}, \frac{1}{2})$ intensity is easily detected earlier by video LEED. The $(\frac{1}{2}, \frac{1}{2})$ beams sharpen and gain intensity as the Pd coverage increases, reaching a maximum at 0.55 ± 0.05 ML (the LEED I-V determination by Wu *et al.*¹⁰ is consistent with this coverage). By this point the $(\frac{1}{2}, \frac{1}{2})$ beams are as sharp as the substrate (1×1) beams. Over the next 0.1–0.2 ML the $(\frac{1}{2}, \frac{1}{2})$ intensity decreases only slightly, but the pattern remains sharp. Visual determination of the maximum is therefore quite difficult. The $(\frac{1}{2}, \frac{1}{2})$ spots have broadened and decreased significantly in intensity by 1 ML. We observe a previously unreported $p(2 \times 2)$ LEED pattern near 1 ML of deposited Pd. The $(0, \frac{1}{2})$ intensity (best seen at 133 eV) first appears at just over 0.8 ML and reaches a maximum at 1 ML, dropping off completely by 1.1 ML.

SUMMARY AND DISCUSSION

The maximum in the $c(2 \times 2)$ LEED pattern occurs at 0.55 ± 0.05 ML. The sharpness of the pattern at this coverage is consistent with a well-ordered 1:1 surface alloy of Pd and Cu. The first breakpoint in the Auger ratio curves, observed at just below one half ML coverage, must then be associated with the completion of the surface alloy layer, as suggested by Wu *et al.*¹⁰ The Auger breakpoint seen near 1 ML is likely associated with the completion of a second mixed layer structure. The corresponding $p(2 \times 2)$ LEED pattern could be due to domains of a (2×1) structure, as has been observed in the case of Au on Cu(100),⁵ or due to a true $p(2 \times 2)$ structure in the surface layer. The structures of the $c(2 \times 2)$ and $p(2 \times 2)$ overlayers are being further investigated by scanning tunneling microscopy and RBS channeling measurements.

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