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## LETTER TO THE EDITOR

# A quantum-well state at the Pd(110) surface

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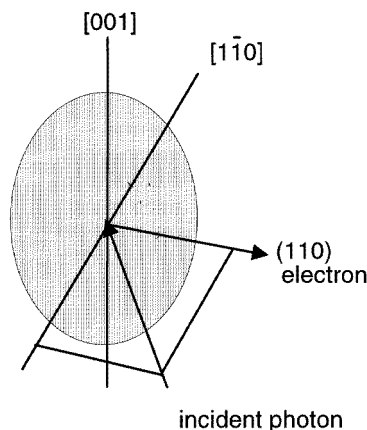
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**Abstract.** Energy versus momentum dispersion relations of Pd(110) along  $\Gamma$ -K-X symmetry lines have been studied using angle-resolved photoemission spectroscopy with synchrotron radiation. We have observed a peak near the Fermi level over the photon energy range of 17–80 eV. We present conclusive data that this peak is a quantum-well state, on this metallic surface, due to the difference in the potential barriers of the surface and bulk. This peak exhibits resonance in intensity with the photon energy, which is well explained by the surface quantum-well model. This is the first observation of electron confinement at the surface of a simple metal.

We provide evidence for a new type of quantum-well state on the Pd(110) surface. The presence of such a state is potentially quite important in studying interfaces and multilayer coupling in, e.g., magnetic multilayer systems [1], since this state can be another state with which to control the multilayer coupling. Our observed state is confined within the top layer surface so that it is distinguishable from the surface barrier resonance found on the Al(111) surface [2]. A quantum-well state in a simple metal system has not been reported so far, though some metal overlayers [3] or superlattices on different metal surfaces [4] show the confinement of electrons due to the mismatch of the band structure. The interesting question that is in our consideration, is the possibility of the presence of the quantum-well state at the simple metal surface. In considering the elementary photoemission process, the photoemitted electrons feel the crystal inner potential when they come out of the surface [5]. If this surface potential undergoes the change abruptly along the surface normal, it is expected that the electrons can be confined at the surfaces. The surface of Pd(110) does not show any reconstruction, unlike the similar transition metal (110) surfaces of Au, Pt and Ir. This suggests that the surface atoms lie in a strongly corrugated potential which is closely related to the sp charge density [6]. Also, there is still a controversy in the possible surface layer disorder at this surface relative to the bulk [7, 8]. These experimental results, however, raise the possibility that the Pd(110) surface should be treated with different potential energy characteristics compared to the surfaces of other metals.

Angle-resolved photoemission studies were performed at the Wisconsin Synchrotron Radiation Center. We employed an angle-resolved hemispherical energy analyser on top of a three-axis goniometer. The base pressure of the chamber was below  $7.0 \times 10^{-11}$  torr during the experiment. We obtained a clean surface by *in situ* Ar<sup>+</sup> sputtering and subsequent annealing up to 800 °C. This process is sufficient to obtain a good  $1 \times 1$  low energy electron diffraction (LEED) pattern. We flashed the sample to 400 °C every 5–6 spectra to remove

small amounts of hydrogen which is believed to cause the small bump around 8 eV after two hours of exposure at low ( $10^{-10}$  torr) pressure. We found that the peak near the Fermi energy was sensitive to hydrogen contamination.

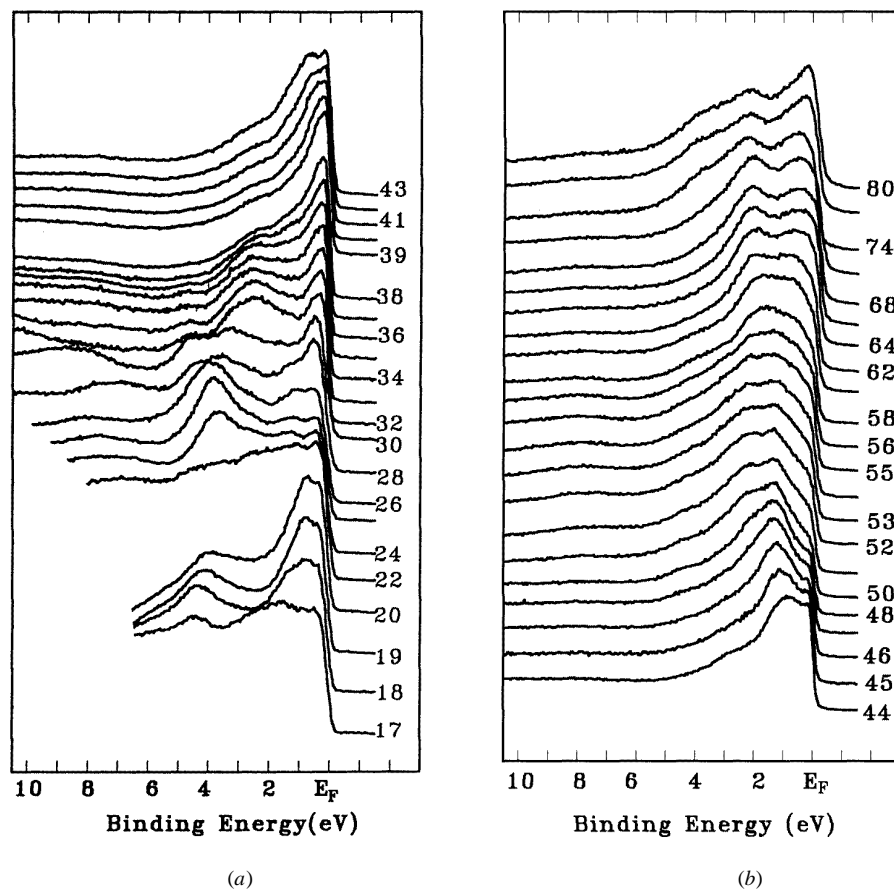


**Figure 1.** The experimental setup of the sample and incident photon in ARPES; all the data represented here are the normal emission spectra.

Figure 1 shows the experimental geometry employed in our measurement. The angle of incidence is  $40^\circ$ . Figure 2 shows the normal emission spectra taken along the  $\Gamma$ -K-X symmetry line, including the photon energy range of (a) 17–43 eV and (b) 44–80 eV. All spectra are normalized to the maximum count rate in each spectrum. It is noteworthy that there is a peak about 0.3 eV below the Fermi energy, clearly observable especially at the photon energy of 44–45 eV. This peak is reported by Yagi *et al* [9] at low photon energies, where they simply attribute the origin of this peak to be a surface related peak or final state effect.

Figure 3 provides the binding energy versus momentum perpendicular to the surface of the features observed in figure 2 based on the free electron final state. The major difference compared with the previous report [9] is that there is no flat band-like peak in our data, except for the 0.3 eV peak previously mentioned. The solid line is the calculation by Christensen using the relativistic augmented plane-wave method [10]. The band structure does not indicate that there is a peak at a binding energy of 0.3 eV, observable for essentially all spectra. This feature meets the three tests for a surface-related feature. First, it is very sensitive to hydrogen adsorption; the adsorption of less than 0.5 Langmuir of hydrogen reduces the peak intensity by over 50%. This is also an indication that it is not a hydrogen-induced state. Also the binding energy is independent of the electron momentum perpendicular to the surface. Finally, the state at 0.3 eV binding energy does not appear in the calculation of the bulk electronic structure, but there does appear to be a gap in the bulk density of states in which a surface-related feature could reside.

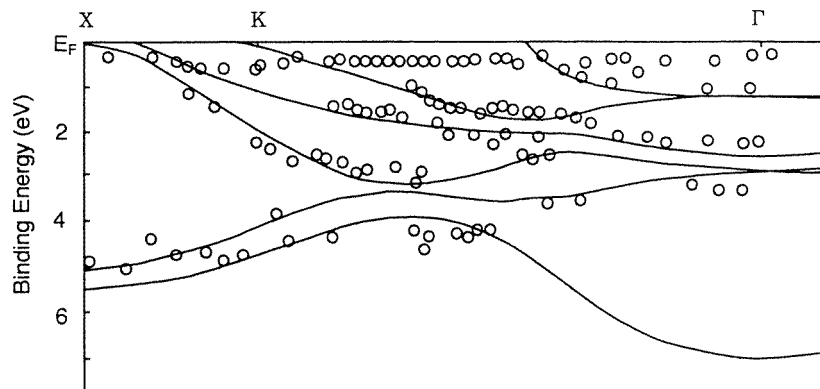
To calculate the intensity of this 0.3 eV peak, we have fixed its position and FWHM and integrated its intensity to fit the intensity lower than 0.3 eV in binding energy. The intensity that we have taken from the spectra contains the contribution from the d band of Pd. However at the photon energy of 30–50 eV, *there is no d band crossing over the Fermi level*. Also the positions of the Fermi level crossing of this d band expected from the band calculation are near the minimum value of the intensity. So our integrated intensity



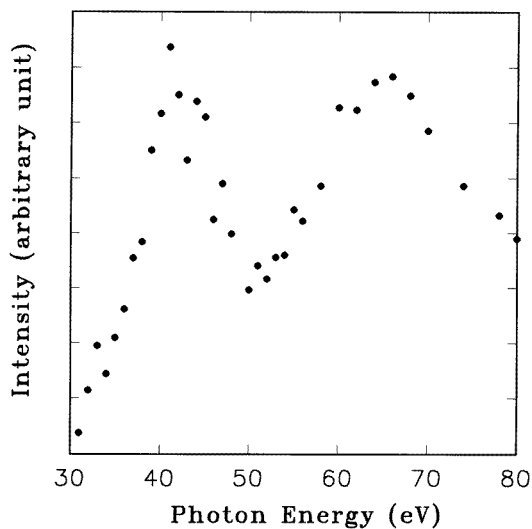
**Figure 2.** The normalized photoemission spectra of Pd(110) for various photon energies. The photon energy range in (a) is from 17 to 43 eV, and in (b) is from 44 to 80 eV. The photon energies are marked on the right side of each spectra. The photon energy of unmarked spectrum is half of sum of adjacent energies.

variation has another origin since the Pd 4d contribution is relatively small. The intensity of this 0.3 eV state versus photon energy is shown in figure 4. There exist two maximum intensity positions at the photon energies of 41.5 and 66.8 eV after the curve fitting of the experimental data. It has been quite puzzling that the location of these positions are unpredictable. The data are not consistent with a final-state effect due to the band gap above the Fermi level [11], which can be checked with Christensen's band calculations at low photon energies. *The data are also inconsistent with a classic surface state*, because the intensity maxima do not correspond to the edges of the Brillouin zone, where the gap opens [12]. Also the resonance of this state cannot be explained with the above possibilities including surface resonance.

We have considered several possible explanations for our data including the intensity maximum positions. As noted above, the 0.3 eV feature is neither due to a final-state effect, nor is it a surface state. Recently, however, another possibility has been developed by several authors: a quantum-well state. Miller *et al* [3] reported a quantum-well state for Ag metal overlayers on Au(111) surface. A quantum-well state found in Co on Cu(100) by



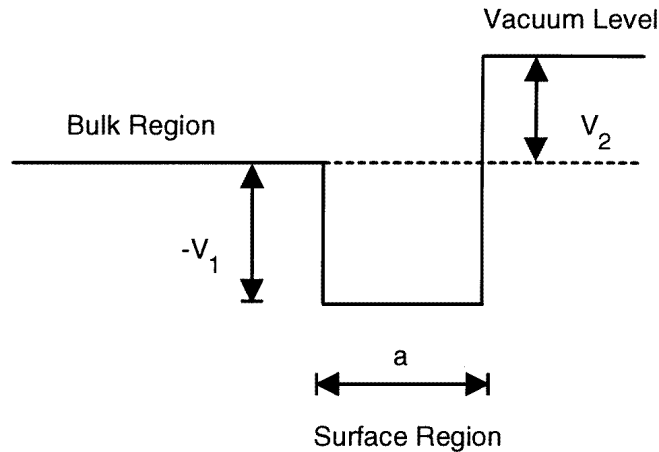
**Figure 3.** The band dispersion of Pd(110) along  $\Gamma$ -K-X symmetry line. The solid line is the data from Christensen's calculations [10].



**Figure 4.** Peak (0.3 eV below Fermi level) intensity versus photon energy.

Himpsel [4] and Ortega and Himpsel [4] is due to the fact that the higher-lying *s*, *p* bands in Co act as a barrier in the average potential relative to the noble metal. McMahon *et al* [13] have shown that the double quantum well can be coupled by varying the interlayer thickness. So far these quantum-well states at the two compositionally modulated systems are due to mainly band gap mismatch. With the possibility of the quantum well state in mind, we think that in our case of Pd(110), the surface potential barrier could be different from that of the bulk. Tamura and Feder [14] suggested that the dynamical surface potential barrier ( $U$ ) would depend on the depth ( $z$ ) of the electron inside the crystal and its energies ( $E$ ) to explain the surface states observed in inverse photoemission spectra [15, 16].

We analysed our data with the surface potential well model in which the surface potential can be varied from the bulk. To calculate the resonance position of the intensity of the 0.3 eV feature, we assumed that the surface potential barrier height might be different from the



**Figure 5.** Schematic description of our surface well model. The potential barrier of the bulk is referenced as zero. The width of the surface region is the effective thickness of the potential barrier with surface value.

bulk potential barrier height. Figure 5 illustrates our model. The surface potential barrier, compared to the bulk barrier, is presented as  $-V_1$ , while  $V_2$  represents the vacuum level with respect to the bulk potential barrier. With this, we can calculate the phase change at the interface versus energy of electrons. This problem has been solved with a numerical method. This model has three adjustable parameters with which to fit the data of figure 4, while the values of  $a$  and  $V_1$  mainly determine the positions of the resonance. A best fit is obtained for the values of  $a = 2.62 \pm 0.5 \text{ \AA}$  and  $V_1 = 7.9 \pm 0.7 \text{ eV}$ . Using these values of the parameters, we can fit the photon energies of the two resonance maxima (41 and 64 eV). The value of  $a$  is quite comparable to the thickness of the top layer of Pd(110) surface. Further, the value of the potential barrier agrees quantitatively with the value used by Tamura and Feder. By varying both  $a$  and  $V_1$ , we find that there are bound states provided that there is a surface potential barrier at least one atomic layer thick. Recent controversy of the possible surface layer disorder may originate from the neglect of this potential barrier difference in their analysis of experimental data. We can conjecture that the origin of the surface potential barrier is related to the surface relaxation. Recently Feibleman [17] has shown that this surface shows anisotropic surface stress. To balance this stress, the top layer has been contracted into the bulk crystal by 10%. The competition between electrostatic attraction and kinetic-energy-related repulsion actually determines the different behaviour at the surface. If the electrons are contracted compared with that of the bulk value, the potential which determines the atoms' position will be deeper than that of the unrelaxed surface.

By studying normal emission spectra of the Pd(110) surface, we have observed an electronic state not predicted by bulk band structure. Of the models in the literature, the one that agrees quantitatively with our data is the model of quantum confinement by the presence of a surface potential. We emphasized that our experimental results are, to our knowledge, the first demonstration that a difference in the surface potential compared to the bulk can be large enough to lead to the quantum confinement of the electrons at the surface. This is believed to be due to the uncommon surface relaxation at this Pd(110) surface. The width and depth of this surface potential are physically reasonable and imply

that Pd(110) will exhibit markedly different interfacial properties than those expected from the bulk potential.

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