the incommensurable displacement profile (1):

$$I_\alpha \propto \sum_k \int_{-\infty}^{+\infty} \langle P_{\alpha\vec{k}}(0) P_{\alpha\vec{k}}(t)\rangle e^{i\omega t} dt, \qquad \alpha = A, \varphi. \tag{5b}$$

Using the fluctuation-dissipation theorem, one finds the amplitudon contribution I_A as

$$I_A \propto \frac{kT}{\kappa^{3/2}} \frac{\Gamma_A}{[2A(T_I - T)]^{1/2}}, \quad T < T_I, \tag{5c}$$

and the phason contribution $I_\varphi > I_A$ as

$$I_\varphi \propto (kT)\kappa^{-3/2}\Gamma_\varphi/\Delta. \tag{5d}$$

Here Δ = const is the gap in the phason spectrum, and Γ_α the damping of the harmonic-oscillator-like phason and amplitudon modes. We assumed that $\omega_A(\vec{k}=0)$ and Δ are much larger than the nuclear Larmor frequency ω_L. If, however, $\Delta < \omega_L$ one finds $I_\varphi \propto \omega_L^{-1/2}$. For Raman processes, on the other hand, we have

$$T_1^{-1}(x) \propto [x^4 J_A + (1-x^2)^2 J_\varphi], \tag{6a}$$

where the spectral densities J_α are always independent of ω_L:

$$J_\alpha \propto \frac{(kT)^2}{\kappa^{5/2}}\left[1 - 2\left(\frac{\omega_\alpha(\vec{k}=0)}{\omega_\alpha(\vec{k}_{\max})}\right)^{1/2} + \dots\right], \qquad \alpha = A, \varphi, \tag{6b}$$

and where the frequencies ω_α are given by expressions (2a) and (2b). Here too J_A decreases with increasing $(T_I - T)^{1/2}$ whereas J_φ is not critically temperature dependent and—except at $T = T_I$—is larger than J_A.

The observed x dependence of T_1 seems to give a better fit with the "direct" than the "Raman" mechanism though no definite conclusions can be made.

The x dependence of T_1 also allows us to determine I_A and I_φ separately. I_A continuously decreases on cooling from T_I into the C phase, whereas I_φ is temperature independent in the I phase and changes discontinuously at T_c. A comparison between the experimental and theoretical ^{87}Rb T_1 data in the I phase of Rb_2ZnCl_4 thus demonstrates the existence of a phason contribution which is—for $x = 0$—rate determining over the whole I phase. The Larmor frequency independence of T_1 shows the presence of a small gap Δ—which is somewhat larger than ω_L—in the phason spectrum. An analogous phason mode has been observed by ^{87}Rb spin-lattice relaxation as well in Rb_2SnBr_4.[7]

[1] A. Janner and T. Janssen, Phys. Rev. B 15, 643 (1977); P. M. de Wolf, Acta Crystallogr. A33, 493 (1977).

[2] A. D. Bruce and R. A. Cowley, J. Phys. C 11, 3609 (1978).

[3] M. Wada, A. Sawada, and Y. Ishibashi, J. Phys. Soc. Jpn. 45, 1429 (1979).

[4] R. A. Cowley, in *Proceedings of the Fourth European Physical Society General Conference; Trends in Physics, York, England, 1978* (European Physical Society, London, 1979), Chap. 3, p. 176.

[5] K. Gesi and M. Iizumi, J. Phys. Soc. Jpn. 46, 697 (1979).

[6] R. Osredkar, S. Južnič, V. Rutar, J. Seliger, and R. Blinc, to be published.

[7] R. Blinc, V. Rutar, J. Seliger, S. Žumer, Th. Rasing, and I. P. Aleksandrova, to be published.

[8] M. Iizumi, J. D. Axe, G. Shirane, and K. Shimaoka, Phys. Rev. B 15, 4329 (1977).

Photoemission Observation of the Formation of Pd(111) Surface States (Surface Resonances) and Resonant *d* Levels for Pd Overlayers on Nb

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Photoemission indicates that the formation of the surface states (surface resonances) on the (111) face of ultrathin Pd overlayers on a recrystallized Nb foil commences with the deposition of the third atomic layer and is completely established at the full fourth layer. It also shows the formation of two resonant *d* states at submonolayer coverages, corresponding to the interaction of Pd *d* levels with the Nb bulk bands and to the Pd bulk *d*-band resonance, respectively.

The observation of intrinsic surface states (surface resonances) has become fairly common on metals[1-4] as well as on semiconductors.[5] To date, by the use of advanced experimental and theoretical techniques, much progress has been made in understanding the origin and character of the intrinsic surface states (surface resonances). Nonetheless, a fundamental question still remains unanswered. That is, at what lower limit of the bulk thickness and of the surface size will the surface states cease to exist? No experimental attempt has ever been made to answer this question, and only a few theoretical calculations exist which provide indirect answers. Gay, Smith, and Arlinghaus[6] have shown that, for Cu(100), *three layers* were *not* sufficient to generate surface states. Only when they later performed an *eleven-layer* self-consistent calculations[6] did they find surface states (surface resonances) near the top of the Cu d band.[4] Louie,[7] on the other hand, has predicted the existence of surface states (surface resonances) on the (111) face of Pd in a *seven-layer* self-consistent pseudopotential calculation. Using the same computational scheme, Kerker, Ho, and Cohen[8] have been able to explain with a *five-layer* calculation the surface resonances observed on the (100) face of Mo.[1]

In the present phoeoemission studies of ultrathin Pd(111) overlayers evaporated onto the (110) face of a recrystallized Nb foil, we show that surface states (surface resonances) not only exist on the (111) face of Pd, contrary to the report by Dahlbäck, Nilsson, and Pessa,[9] but also appear at the moment when the third atomic layer begins to pile up. Upon completion of the fourth atomic layer, the surface states (surface resonances) are fully established and the corresponding photoemission spectrum is similar to that of single-crystal Pd(111).[10]

Photoemission energy distributions (PED's) were measured in an ultrahigh vacuum for unpolarized He I radiation ($h\nu = 21.2$ eV) using a double-pass cylindrical-mirror analyzer (CMA).[11] The angle of incidence was about 70° and the axis of the CMA was about 6° off the surface normal. Ultrathin Pd layers were obtained *in situ* by evaporation, using a W-basket Pd evaporator, onto a clean, flashed Nb(110) substrate which was recrystallized[12] from a thin (50 μm) Nb foil by repeatedly heating to 2200 °C. The deposition of Pd atoms on the (110) face of Nb exhibits a LEED (low-energy electron diffraction) pattern corresponding to the (111) face of Pd at more-than-one-monolayer coverages.[13]

Deposition of Pd atoms is quoted in terms of the average number of monolayers, $\bar{n}$, which was estimated based on the evaporation time, the PED, the change in the work function, and the Auger intensity in a self-consistent framework. In order to determine the evaporation time needed to obtain a single monolayer, we have taken advantage of the fact that hydrogen readily adsorbs on Nb(110) and induces a pronounced level at 5.4 eV below the Fermi level ($\epsilon = -5.4$ eV),[11] quite different from that of H on Pd(111).[10] After evaporation, the specimen was exposed to H_2 up to saturation [about 10 L (1 L $= 10^{-6}$ Torr sec)]. PED's were then taken and the intensity of the characteristic energy level of H on Nb(110) was measured. The results are shown in Fig. 1 where we have plotted the characteristic H/Nb(110) peak intensity as a function of Pd evaporation time. The decrease of H-photoemission intensity with evaporation time is apparently due to the removal of available H-adsorption sites by Pd atoms. For evaporation times greater than 16 min, no H-induced peak at $\epsilon = -5.4$ eV is observed, suggesting that a full monolayer of Pd atoms is obtained with 16 min of evaporation. The fact that the available H-adsorption sites decrese *linearly* with coverage suggests strongly that no significant stacking growth occurs during the evaporation. Moreover, we have also found that the H^+ intensity generated by electron-stimulated desorption of such a $(Nb + Pd + H_2)$ system decreases dramatically with Pd coverage,[14] suggesting that there may be very few H atoms *on* the surface of Pd layers.

Figure 2 shows the PED's for various $\bar{n}$'s of Pd layers and Fig. 3 shows the corresponding work

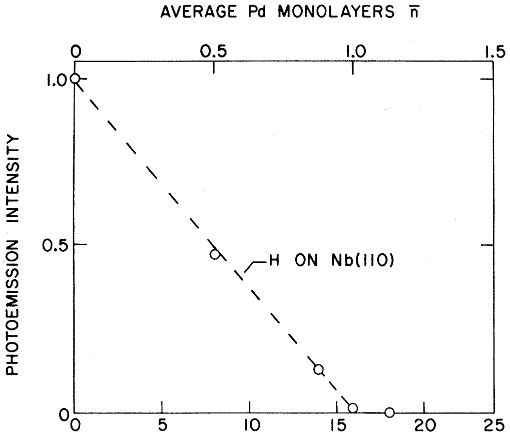

FIG. 1. After Pd was evaporated onto Nb(110), the specimen was exposed to H_2 up to saturation coverage. The photoemission intensity of H on Nb(110) ($\epsilon = -5.4$ eV) was then measured as a function of Pd evaporation time and used as a guide to determine the time needed to obtain one monolayer.

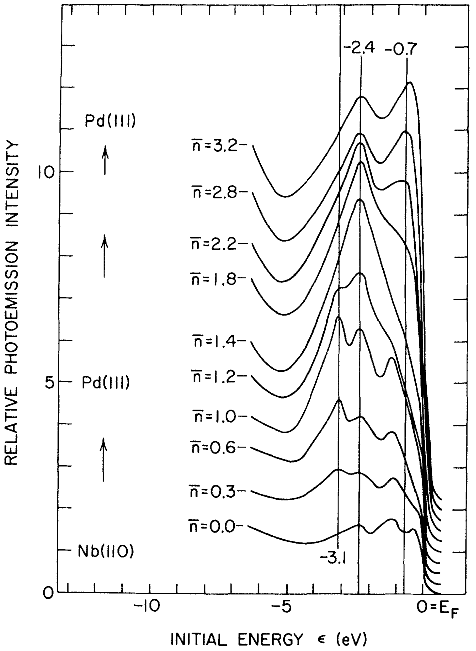

FIG. 2. PED's of various coverages of Pd(111) overlayers on Nb(110). $\bar{n}$ is the average number of Pd monolayers.

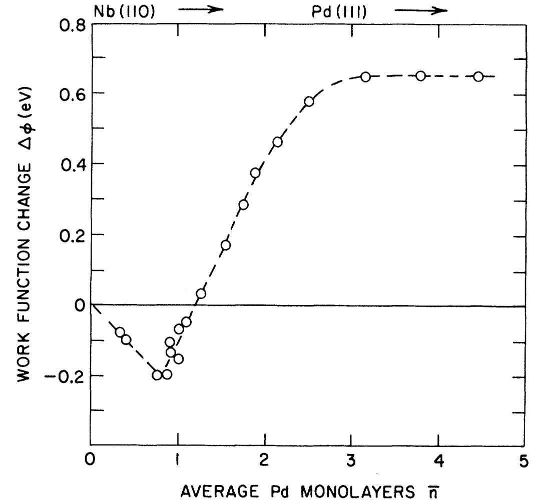

FIG. 3. Work-function changes as a function of $\bar{n}$.

function changes. At submonolayer coverages, the work function decreases linearly and two pronounced energy states are observed. The one at $\epsilon = -3.1$ eV seems to saturate at $\bar{n} = 1$ and is interpreted here as the resonant *d* state[15] due to the interaction of Pd *d* levels with the Nb bulk bands. Another state at $\epsilon = -2.4$ eV is observed to grow continuously, without changing the energy position, with coverage and becomes the predominant *d*-band structure observed in the PED of a clean bulk Pd(111) sample[10] at $\bar{n} > 3$. The work function increases almost linearly after $\bar{n} \simeq 0.9$ and then reaches a saturation value at $\bar{n} \geq 3$. Angular dependences indicate that the state at $\epsilon = -2.4$ eV is different from the *d*-band peak of the Nb substrate at the same initial energy. These results suggest that the state at $\epsilon = -2.4$ eV at submonolayer coverages is characteristic of Pd overlayers. In view of the previous conclusion that no significant stacking growth occurs during the submonolayer evaporation, we interpret the state at $\epsilon = -2.4$ eV as the initial formation of Pd bulk *d* bands due to the presence of one-layer-thick clustered Pd islands. It is not clear whether the individual Pd atoms within the islands are in registry with the Nb(110) substrate or in the form of Pd(111) mesh. LEED optics study tends to support the former configuration.[13] This, however, would imply that the energy position of the Pd bulk *d*-band resonance is insensitive to the change of the Pd-Pd distances by even up to a factor of 10%.

The most significant and perhaps the most important phenomenon occurs at $\bar{n} > 2$ where we observe a new state emerging from the shoulder at $\epsilon = -0.7$ eV. (The shoulder appears at $2 > \bar{n} > 1$.) Its intensity increases rapidly with coverage and saturates at $\bar{n}$ roughly equal to 4. This result is shown in Fig. 4 where we have plotted the intensity of this state as a function of average Pd monolayers. We have found that the state at $\epsilon = -0.7$ eV is very sensitive to contamination. Indeed,

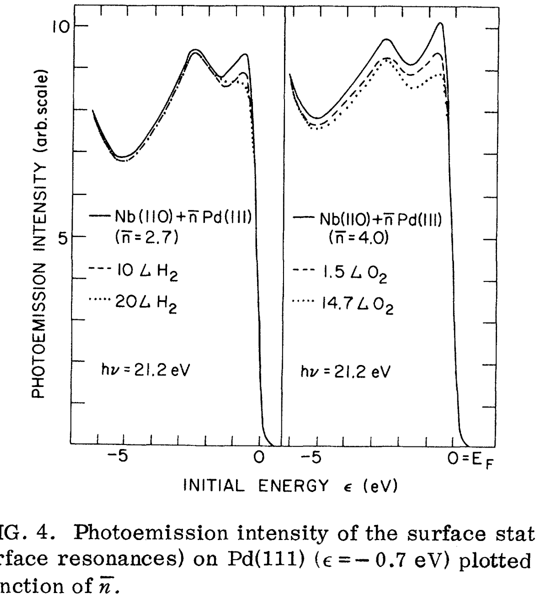

FIG. 4. Photoemission intensity of the surface states (surface resonances) on Pd(111) ($\epsilon = -0.7$ eV) plotted as a function of $\bar{n}$.

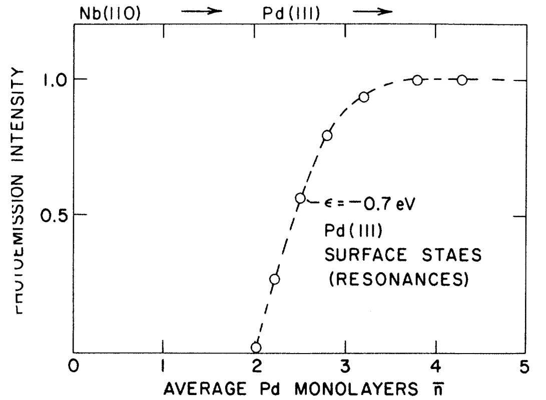

FIG. 5. PED of $\bar{n}$ monolayers of Pd(111) on Nb(110) with and without H_2/O_2 exposure.

the adsorption of oxygen and hydrogen removes this state. Figure 4 shows this effect for various coverages. We interpret this as a surface state (surface resonance). This interpretation is consistent with a self-consistent pseudopotential calculation[7] which shows that surface states (surface resonances) do exist on the (111) face of Pd at initial energies around $\epsilon = -0.7$ eV, and in the outer half of the surface Brillouin zone, which is roughly the region from which we collected the photoelectrons.

It is seen from Fig. 5 that hydrogen removes only the surface state (surface resonance), whereas oxygen also attenuates the d-band emission. Furthermore, the hydrogen-adsorbed PED does not exhibit new states within 7 eV below the Fermi level and the PED itself is similar to that of $\bar{n} = 2$ without contamination. Indeed, the PED's of $\bar{n} = 2$ with and without hydrogen exposure are almost identical to each other. These results suggest that the PED of $\bar{n} = 2$ is essentially due to bulk-band properties. Only when $\bar{n} > 2$ can and do the surface states (surface resonances) show up.

The result shown in Fig. 4 thus presents a conclusive answer to the question of when a surface state (surface resonance), which is localized at the solid-vacuum interface, starts to form or ceases to exist. The present result indicates that the surface states (surface resonances) on the (111) face of bulk single-crystal Pd will cease to exist when the thickness of the bulk solid becomes less than the equivalent of two full atomic layers. (In the present case, only one side of the Pd thin film is adjacent to the vacuum.) More specifically, the result shows that the surface states (surface resonances) on the (111) face of Pd begin to be observed at the moment when the third atomic layer starts to pile up. With increasing coverage, the surface states grow up rapidly and become fully established at the completion of the fourth layer. At $\bar{n} = 4$, the PED is essentially identical to that of single-crystal Pd(111).

In conclusion, the present photoemission results indicate the existence of surface states (surface resonances) on the (111) face of ultrathin Pd overlayers, in agreement with the prediction of theory.[7] In addition, the results indicate that the formation of these surface states (surface resonances) commences with the deposition of the third atomic layer and is completely established at the full fourth overlayer. The results have also shown the formation of two resonant d states at submonolayer coverages, corresponding to the interaction of Pd d levels with the Nb bulk bands, and the Pd bulk d-band resonance, respectively.

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[1] Shang-Lin Weng, E. W. Plummer, and T. Gustafsson, Phys. Rev. B 18, 1718 (1978), and Phys. Rev. Lett. 39, 822 (1977).

[2] P. O. Gartland and B. J. Slagsvold, Solid State Commun. 25, 489 (1978), and Phys. Rev. B 12, 4047 (1975).

[3] P. Heimann, H. Neddermeyer, and H. F. Roloff, J. Phys. C 10, L17 (1977).

[4] P. Heimann, J. Hermanson, H. Miosga, and H. Neddermeyer, Phys. Rev. Lett. 42, 1782 (1979).

[5] J. A. Appelbaum and D. R. Hamann, Rev. Mod. Phys. 48, 479 (1976).

[6] J. G. Gay, J. R. Smith, and F. J. Arlinghaus, Phys. Rev. Lett. 38, 561 (1977), and 42, 332 (1979).

[7] S. G. Louie, Phys. Rev. Lett. 40, 1525 (1978).

[8] G. P. Kerker, K. M. Ho, and M. L. Cohen, Phys. Rev. Lett. 40, 1593 (1978).

[9] N. Dahlbäck, P. O. Nilsson, and M. Pessa, Phys. Rev. B 19, 5961 (1979).

[10] J. E. Demuth, Surf. Sci. 65, 369 (1977).

[11] R. J. Smith, to be published.

[12] M. A. Pick, J. W. Davenport, M. Strongin, and G. J. Dienes, Phys. Rev. Lett. 43, 286 (1979).

[13] The same result has also been obtained in a more detailed LEED study by M. El-Batanouny, M. Strongin, and M. A. Pick (to be published).

[14] Shang-Lin Weng, to be published.

[15] D. E. Eastman and W. D. Grobman, Phys. Rev. Lett. 30, 177 (1973).