

BNL--35988

BNL 35988

DE85 009822

CONF-841157--88

VUV SYNCHROTRON LIGHT AS A TECHNIQUE FOR STUDYING THE INTERFACE QUALITY AND PROPERTIES OF THIN OVERLAYERS

M. W. Ruckman, V. Murgai, and Myron Strongin
Physics Dept., Brookhaven National Laboratory, Upton, New York 11973 USA

MASTER

December 1984

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

The submitted manuscript has been authored under contract DE-AC02-76CH00016 with the Division of Materials Sciences, U.S. Department of Energy. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

VUV SYNCHROTRON LIGHT AS A TECHNIQUE FOR STUDYING THE INTERFACE QUALITY AND PROPERTIES OF THIN OVERLAYERS

M. W. RUCKMAN,* V. MURGAI,** and MYRON STRONGIN
 Brookhaven National Laboratory, Physics Dept., Upton, N.Y. 11973

ABSTRACT

The measurements presented here show the value of synchrotron light for determining both the electronic structure of overlayers, and the physical nature of the overlayer-substrate interface. A comparison is given between deposited layers and thermally stabilized layers. Estimates are also made of the bonding energy between the overlayer and substrate.

Introduction

In this paper we wish to indicate some of the ways that synchrotron radiation can be used to study the properties of metal overlayers in a rather straightforward way. The properties of Ni, Pd, and Pt layers on the Ta(110) surface will be used to illustrate the features of this technique. These particular systems are of great interest since in the case of Pd overlayers on Nb, which has been studied in detail[1,2,3] the hybridization of the overlayer with the underlying substrate causes drastic changes in the layer properties, and this in turn causes dramatic changes in the chemical properties.[1,2,3,4] The combination of electronic structure measurements and core level shifts are used to estimate the bonding energy of Pt on Ta.

Experimental

The experiments were carried out on recrystallized Ta foils which crystallized in the (110) orientation. The metals were evaporated from tungsten baskets, except for Pt which was made into a coil and then directly heated by passing current through it. The core level measurements were made using tunable radiation provided at NSLS. The spectra were measured with a double-pass cylindrical mirror analyzer. Some of the valence band spectra were taken with a laboratory He lamp. The resolution of the measurements using synchrotron radiation was essentially determined by the Plane Grating Monochromator (PGM) which, at present has a resolving power of about $\Delta E/E=150$.

Data

Valence Band Spectra in Fig. 1 and 2, we show the angle integrated valence band photoemission spectra taken for Ni and Pd, and Pt layers, and in addition we show results for thermally treated layers. The data show that in all cases the states of the overlayer metal hybridize with the substrate and appear below E_F . In the case of Ni this is less apparent, but difference curves verify that the initial Ni states appear below E_F . Pd initially grows in a commensurate overlayer on both Nb [1] and Ta, then becomes incommensurate with a (111) FCC structure from one to 1.2 layers and finally grows as (111) Pd as more Pd is added. When a thicker Pd layer is heated most of Pd goes into the Ta or Nb and there is a temperature range from 700 to 900C where a stable "commensurate" monolayer of Pd exists on the surface. Ni and Pt also appear to grow commensurately although there is some evidence of mismatch in the LEED pattern, finally become incommensurate, and

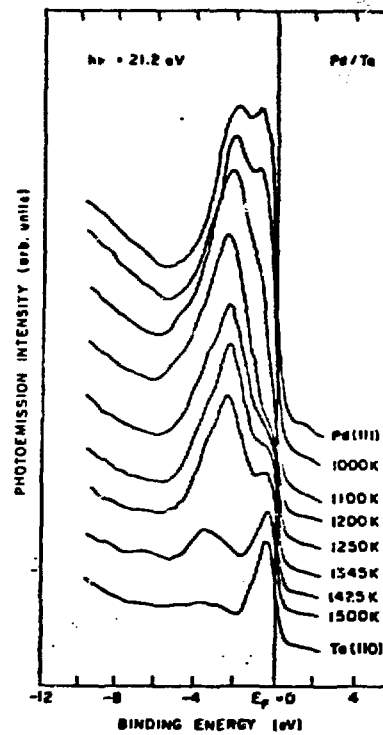
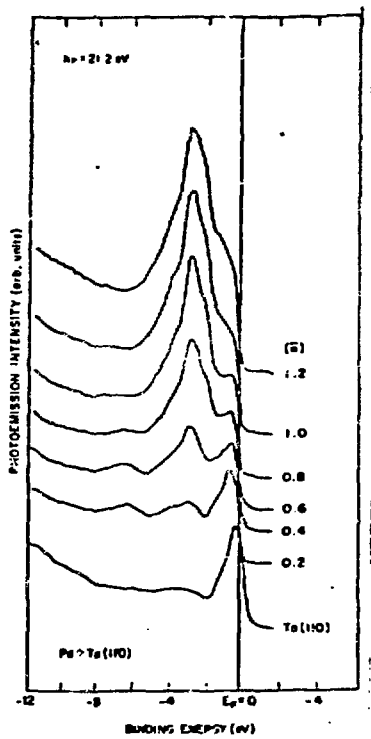


Fig. 1 (a) Energy distribution curves of Ta(110) and Pd films of increasing coverage on Ta(110). Photoemission spectra were taken using HeI (21.2 eV) VUV radiation. (\bar{n}) denotes the approximate palladium coverage (1.0 = a monolayer). (b) Data for thermally stabilized films, annealing temperature is at right.

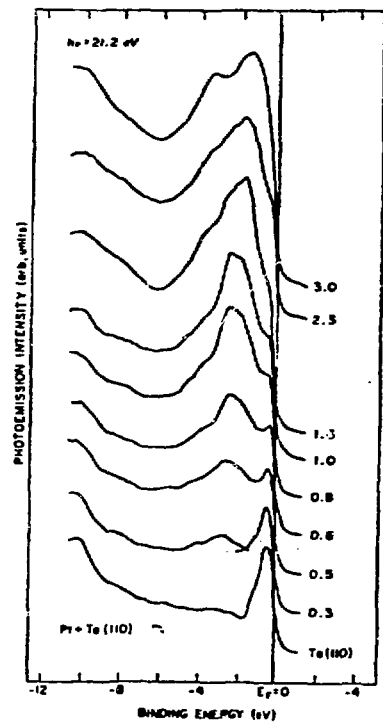
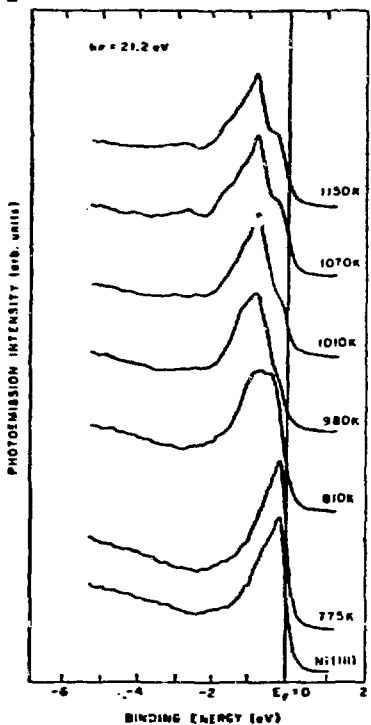


Fig. 2 (a) Energy distribution curves for thermally stabilized Ni films on Ta(110) taken using HeI (21.2 eV) radiation. Annealing temperatures are given on the figure. (b) Pt films on Ta(110). Approximate Pt overlayer coverages shown on figure ($n = 1.0$ is = monolayer coverage).

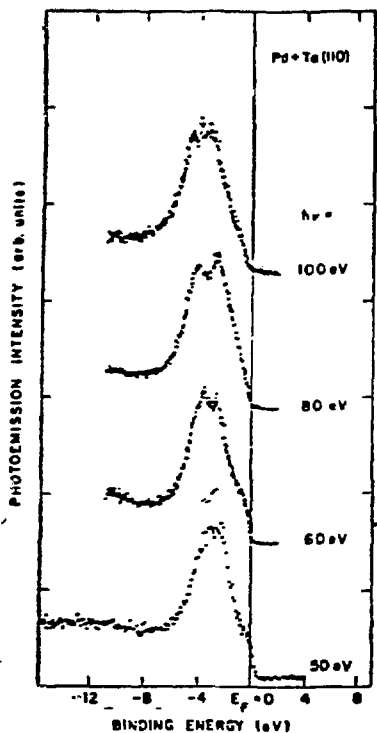


Fig. 3. Energy distribution curves taken using synchrotron radiation for a palladium "monolayer" on Ta(110) produced by thermal stabilization. Note the absence of states at E_F for $h\nu = 80$ and 100 eV.

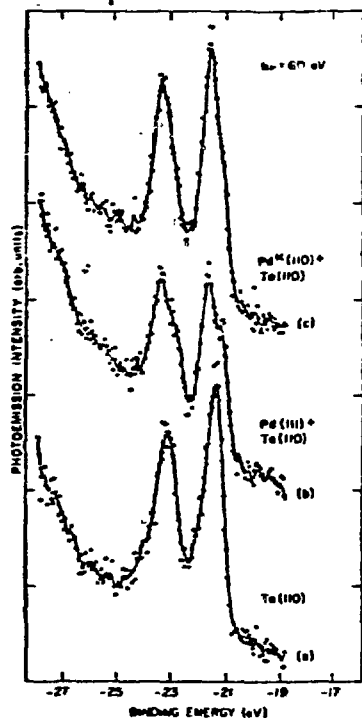


Fig. 4. Ta 4f core levels for (a) clean Ta(110), (b) approximate monolayer Pd coverage and (c) thermally stabilized Pd "monolayer" on Ta(110) at $h\nu = 60$ eV.

then form a (111) oriented FCC layer for thicker films. When a Ni(111) layer is heated on Ta there is a temperature range where it forms a stabilized layer with a C(2x2) structure on Ni(111). Fig. 2a shows that the d bands of this "surface compound" have a large component below E_F , and are lower than in the monolayer deposited film. Data for Pt are shown in Fig. 2b.

The features shown above are easily obtainable with a discharge lamp and do not require the use of synchrotron radiation. However synchrotron radiation allows the study of cross section dependence which facilitates unraveling which features belong to which element. For example the feature near E_F in Fig. 1 are thought to be Ta states from the underlying layers, and actually the density of Pd states is quite small at E_F . In Fig. 3 we show that by going to higher photon energies where the Ta cross section is reduced relative to the Pd cross section, that the states at E_F are greatly reduced relative to the features below E_F and hence have mostly Ta like character. This technique can be developed in a more general way to determine the symmetry of various surface orbitals.[5]

Core Level Spectra

The major subject of interest here, and which has great value for determining the qualities of the film and film substrate interface are the core level spectra. In this regime of energies, synchrotron radiation is unique. The case studied here involves metal overlayers on Ta, and we have chosen to use the 4f levels of Ta as the major probe of interface quality. Pt also has sharp 4f levels, and in this case both the substrate and overlayer core levels can be studied. The 4f core levels of Ta are shown in Fig. 4(a).

We have previously mentioned that a monolayer of Pd deposited on Ta(110) grows commensurately on the surface. It then becomes incommensurate with the Ta(110) surface, and remains in the Pd(111) structure as further Pd is deposited. Such a monolayer is shown in Fig. 4(b). In 4(c) a layer made by

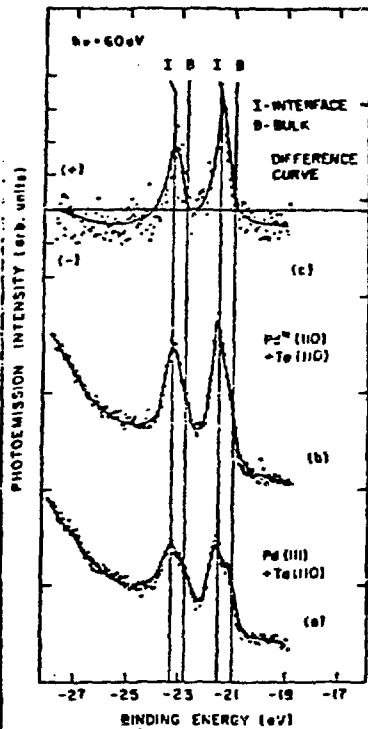


Fig. 5. Comparison of Ta 4f core-levels for (a) approximate monolayer Pd coverage, (b) thermally stabilized Pd layer on Ta(110), (c) difference curve (b)-(a) at $h\nu = 60$ eV.

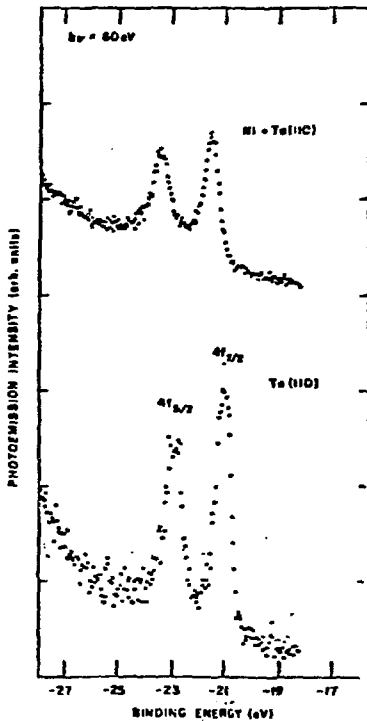


Fig. 6. Ta 4f core level spectra for clean Ta(110) and for Ta(110) with a thermally stabilized Ni overlayer.

heating a thicker Pd layer is shown. For the clean Ta surface only the $4f_{5/2}$ and $4f_{7/2}$ peaks are apparent. (Any surface core level shifts are not resolved here.) When Pd is added two doublets are now apparent, those from clean Ta and also the peaks from the Ta-Pd interface, which are shifted to higher binding energies. It is interesting to note that the peak for the thermally stabilized Pd "monolayer" in Fig. 4(c), shows relatively less pure Ta. In Fig. 5 we show by a difference curve that the relative value of the shifted Ta peak is higher in the thermally stabilized layer. A reasonable interpretation of this result is that in the deposited layer the Pd is strictly in one layer and there is still a strong signal from the clean Ta coming from below the interface layer. In the thermally stabilized layer additional Pd must be in the surface layers, which reduces the clean Ta signal. Hence these results show that the underlying surface region is different in these two cases, even though LEED and Auger indicate somewhat comparable results. Actually while Auger spectra do not show any obvious peak shifts in the Ta peaks there can be slightly different Auger intensities for the two types of layers.

In Fig. 6 we show the core level spectra for clean Ta and a thermally stabilized Ni layer on Ta. In this case, where there is a $C(2 \times 2)$ phase only shifted Ta peaks are observed. This implies that the Ni-Ta compound is several layers thick.

In Fig. 7 the core levels are shown for clean Ta and for different Pt coverages. The Pt-Ta interface is indicated by the shoulder at high binding energy which increases with Pt coverage. The quality of this interface is clearly not as good as the Pd-Ta case because a Ta 4f core component readily attributable to tantalum oxide is clearly visible. In Fig. 8 the Pt 4f levels are shown over the same coverage range. It is evident that at 0.2 ML coverage the greatest shift to higher binding energy is observed. When the Pt coverage reaches 0.4 ML, the shift appears to stay constant up to 1 ML, but it is not at the bulk value. This apparently implies islanding of the Pt and

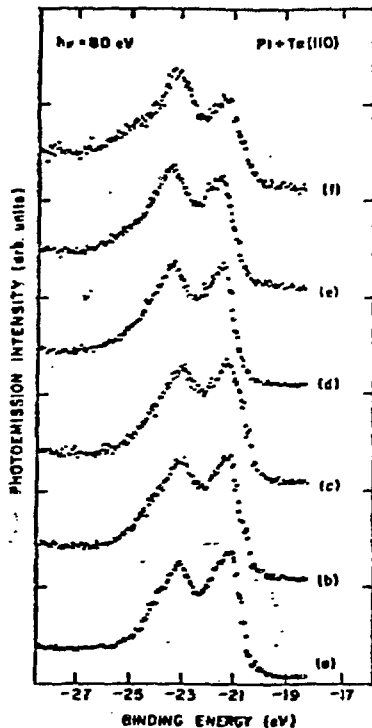


Fig. 7. The Ta $4f_{7/2}$ and $4f_{5/2}$ photoelectron energy distributions for various Pt coverages on Ta(110) Photoemission excited by 80 eV synchrotron radiation. (a) clean Ta(110), (b) 0.2 ML, (c) 0.4 ML, (d) 0.6 ML, (e) 0.8 ML, (f) 1 ML.

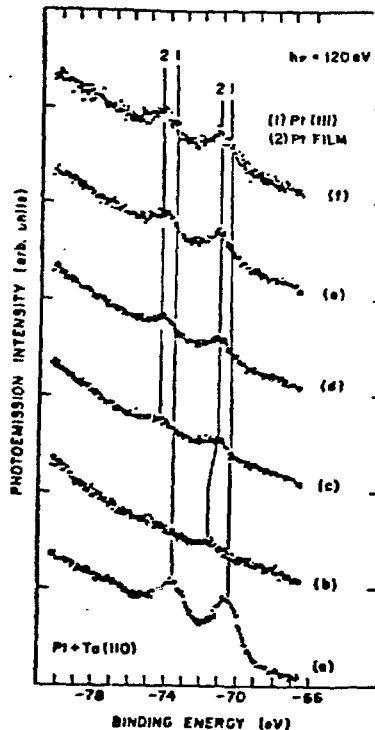


Fig. 8. The Pt $4f_{7/2}$ and $4f_{5/2}$ photoelectron energy distributions for various Pt coverages on Ta(110) photoemission excited by 120 eV synchrotron radiation. (a) clean Pt(111), (b) 0.2 ML, (c) 0.4 ML, (d) 0.6 ML, (e) 0.8 ML, (f) 1 ML.

then the growth of islands from 0.4 ML to 1 ML.

The results for Pt on Ta are of interest for yet another reason. Because there are relatively sharp f levels in both metals, core level shifts can be measured for both substrate and overlayer and some estimate can be made of the binding energy. There is as yet no real prescription for doing this and some assumptions must be made. If it is assumed that the bonding of the overlayer and substrate is due to hybridization of the d-bands, and if further there is no net charge transfer. Then the core levels shifts essentially define the shifts in reference levels when the metals come together, and it is the large shift of the Pt d-bands to lower binding that leads to the major term in the bonding energy. This shift turns out to be greater than the core level shifts which are relatively small. If one goes through this analysis as described by Oelhafen [6] the binding energy is about -1.9 eV/atom. The expression given by Oelhafen for the heat of formation is

$$\Delta H = \int_{\text{band of AB}}^{E_F} (E - E_F) \rho_A^{AB} dE - \int_{\text{band of A}}^{E_B^A} (E - E_F) \rho_A dE + N_A^d \Delta \epsilon$$

and similar terms for B. ΔH is the heat of formation, ρ_A^{AB} is the partial d-band density of states of element A in the alloy AB, N_A^d is the average number of d electrons of element A in the alloy per atom, and $\Delta \epsilon$ is the core level shift. It is clear that the partial density of states can only be

determined when the d bands do not greatly overlap. This assumption is only partially valid in this present case, although the data in Fig. 2b show Pt features which are fairly separate from the Ta d band. Another approach which involves different assumptions, is the work of Johansson and Martenson [7] which is based on a Born-Haber cycle and the equivalent core approximation which assumes that the core ionized Z atom is equivalent to a valence ionized Z+ atom. This method provides a shift of ≈ 0.9 eV for Pt on Ta which is in agreement with the data in Fig. 7. However it was assumed that the difference of the heats of adsorption for Pt and Au on Ta can be approximated by the heats of solution as calculated by Miedema, et al. [8]

Another interesting feature in the data which will not be mentioned here is valence band satellite features in Ni and Pd. Work has been done on the cross section dependence of the 6 eV Ni satellite and the 8 eV Pd satellite as a function of photon energy for both thick layers and monolayers. For the monolayer films the satellite shifts to higher binding energies.

Summary

This work is meant to show the great wealth of information that can be obtained by synchrotron studies of metal overlayer systems. The combination of valence band and core level features allows some estimate to be made of the heat of formation at the interface and the change in electronic states at the interface. Future experiments are also in progress to investigate the chemical properties of these overlayer systems, which are significantly different from either the thick overlayer metal or the substrate.

Acknowledgements

We are grateful to the staff at NSLS and to F. Loeb and R. Raynis for excellent technical support on the U7 beamline. Research is supported by the Div. of Materials Sciences, U.S. DOE under contract DE-AC02-76CH00016.

*Current address: Univ. of Minnesota, Minneapolis, Minnesota 55455.

**Current address: Phys. Dept., Boston University, Boston, Mass. 02215.

References

1. M. Strongin, M. El-Batanouny, and M. Pick, Phys. Rev. B 22, 3126 (1980).
2. M. El-Batanouny, M. Strongin, G. P. Williams, and J. Colbert, Phys. Rev. Lett. 46, 269 (1981); M. Sagurton, M. Strongin, F. Jona, J. Colbert, Phys. Rev. 28, 4075 (1983).
3. J. P. Muscat, Surf. Sci. 131, 299 (1983); V. Kumar and K. Bennemann, Phys. Rev. 28, 3138 (1983); M. El-Batanouny, D. R. Hamann, S. R. Chubb, and J. W. Davenport, Phys. Rev. B 27, 2575 (1983).
4. M. W. Ruckman and M. Strongin, Phys. Rev. 29, 7105 (1984).
5. M. El-Batanouny, M. Strongin, and G. P. Williams, Phys. Rev. B 27, 4580 (1983).
6. P. Oelhafen, Jour. Phys. F: 11, L4 (1981).
7. B. Johansson and N. Martensson, Phys. Rev. B 21, (1980).
8. A. K. Niessen, F. R. de Boer, R. Boom, P. F. de Chatel, W. E. M. Mattens, and A. R. Miedema, Calphad 7, 51 (1983).