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Substrate effects on the electronic structure of metal overlayers—an XPS study of polymer-metal interfaces

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The electronic structures of copper, nickel, and chromium overlayers on polystyrene and polyvinyl alcohol have been investigated with x-ray photoemission spectroscopy. At submonolayer coverages, the peak position and width of the metallic-core levels vary significantly from one substrate to the other. Most of these variations can be accounted for in terms of changes in the atomic and extra-atomic relaxation energies during the photoemission process. Much of this change is brought about when the metal atom deposited on polyvinyl alcohol interacts with the substrate oxygen and forms a metal-oxygen-polymer complex. The presence of this complex is verified by changes in the photoemission line shapes of the substrate carbon and oxygen atoms.

I. INTRODUCTION

In metalizing polymers, the chemical condition of the surface has been found[1] to alter the adhesion characteristics of the metal film. In particular, it has been shown that metal adhesion can be varied by plasma treatment of the polymer surface with oxygen and with other gases.[2-4] In a previous publication,[5] we have identified hydroxl, carbonyl, and ester groups which were created on polymer surfaces during oxygen plasma treatment. We were later able to identify[6] the formation of a metal-oxygen-polymer complex at an interface and correlate its presence with an increase in the adhesion of the metal film.

Other workers[7-14] have studied with photoemission the electronic structure of thin metal overlayers on inorganic substrates. In particular, Tibbetts and Egelhoff[10] found for small metal clusters on a clean, amorphous carbon substrate that all the electronic binding energies increased by about 0.6 eV with respect to the bulk values. They attributed this to either decreased extra-atomic relaxation energies or to an atomic renormalization (expansion) of the valence orbitals. We have attributed[15] analogous changes in the core binding energies of copper atoms on polystyrene to changes in both extra-atomic and intra-atomic relaxation energies.

In this work we describe the results obtained from a study of copper, nickel, and chromium overlayers deposited on polystyrene and polyvinyl alcohol. Using x-ray photoemission spectroscopy we measured significant variations in the core binding energies (~1.5 eV) and line shapes (~2 eV FWHM) as we varied both the metal and the substrate atoms. These changes can be related to differences between the intrinsic properties of the metal atoms as well as to differences in the interaction with the substrates. In the following section, we describe the details of both the experimental preparation and the data acquisition. The third section describes the experimental results and the fourth section discusses in detail the significance of the measurements.

II. EXPERIMENTAL

The interactions taking place on the surface were monitored with x-ray photoemission spectroscopy (XPS) using the same system as described previously.[5,6] This consisted of a commercial[16] double-pass cylindrical mirror analyzer and an Mg $K\alpha$ x-ray source in an ultrahigh-vacuum system whose operating pressure was about 2.6×10^{-8} Pa (2×10^{-10} Torr).

Both the atactic polystyrene and the polyvinyl-alcohol films were solvent cast with a liquid thickness of 0.01 mm and air dried at 22° C. After insertion into the vacuum chamber, the polystyrene was warmed to 140° C for one hour, or the time needed to remove the remaining solvent from the bulk of the film. The polyvinyl-alcohol film was only warmed to 70° C. The clean polymer films were examined with both XPS and infrared (ir) spectroscopy and were found to be free of impurities ($\leq$0.1 atomic %) and to consist of CH_2 and $CH\text{-}C_6H_5$ groups for polystyrene and CH_2 and HCOH groups for polyvinyl alcohol.

Copper and nickel were deposited from metal foil wrapped around a hot tungsten filament. Chromium was evaporated from a chrome-plated tungsten wire. XPS measurements at a resolution of 0.8 eV were made to determine the metal coverage as well as the electronic structure at the interface. The metal coverage was determined by substituting the experimentally measured areas under the XPS curves, core-hole cross sections,[17] an electron mean free path in both the metal[18] and the polymer,[19] and an instrument response function into the equations for emitted electron intensity.[20] At coverages near one monolayer, these values

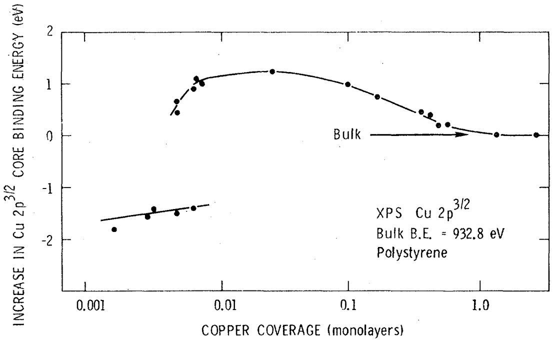

FIG. 1. Variation in the $2p^{3/2}$ electron core binding energy as a function of metal coverage on polystyrene for deposited Cu.

were checked with results from a quartz-crystal thin film monitor.

During photoemission, a small buildup of positive change occurred on the surface, resulting in a shifting of the energy scale by 1.0–2.5 eV. This charging was accounted for by setting the binding energy relative to the Fermi level of the C1*s* electrons to 285.0 eV for carbon atoms involved in CH_2 bonds and referencing the other levels to that value, a method which has been successfully used in the examination of other polymer surfaces.[5,6,12,21] The metal overlayers were verified to be in electrical contact with the substrate, for when a bias voltage was applied to the target assembly an identical energy shift was measured for both overlayer and substrate atoms.

The experimental data was acquired by a dedicated, real-time minicomputer system and stored in digital format. This allowed us to perform accurate profile subtraction, line shape analysis, and curve fitting.

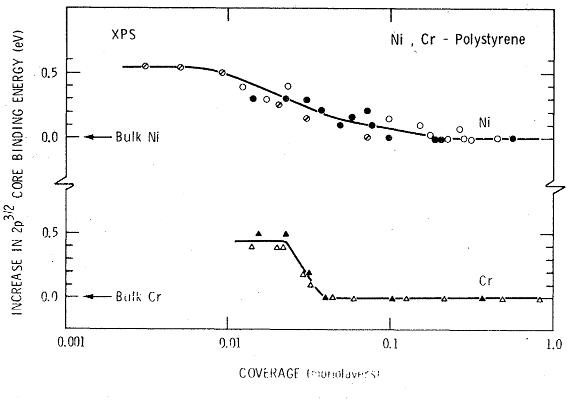

FIG. 2. Variation in the $2p^{3/2}$ electron core binding energy as function of metal coverage on polystyrene for deposited Ni and Cr. The different-labeled points are for separate and independent metal evaporations.

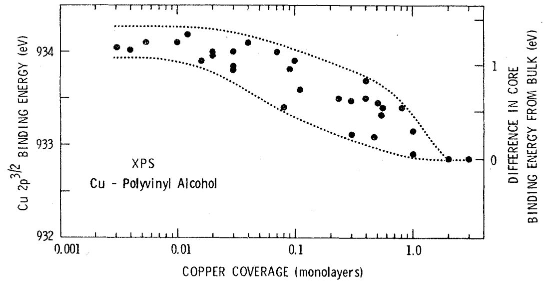

FIG. 3. Variation in the $2p^{3/2}$ electron core binding energy as a function of metal coverage on polyvinyl alcohol for deposited Cu.

III. RESULTS

Copper, nickel, or chromium was deposited on clean polystyrene or clean polyvinyl alcohol at coverages from 0.002 to 10.0 monolayers. At each coverage, the metal $2p^{3/2}$ core electron binding energy was measured with XPS. The peak positions of the $2p^{3/2}$ line shapes for a number of coverages on a number of different samples are plotted in Figs. 1–5.

In comparing the different sets of data, a number of overall differences are striking. First, the Cu-polystyrene interface is the only example of a metal core level having a binding energy less than the bulk value. Second, the data for Cu, Ni, and Cr on polystyrene were all quite reproducible within 0.2 eV, and a single line serves as an adequate aid to the eye. On the other hand, when these same metals were deposited on polyvinyl alcohol, the scatter was often as large as 1.0 eV, with the data forming a broad band. Third, when nickel and chromium were deposited on polystyrene, the bulk value of the $2p^{3/2}$ core energy was reached when the metal coverage was much less than one monolayer. However, when these same metals were deposited on polyvinyl alcohol, the metal coverage needed to be about one monolayer before the bulk

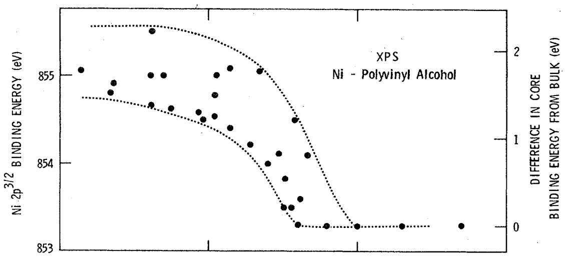

FIG. 4. Variation in the $2p^{3/2}$ electron core binding energy as a function of metal coverage on polyvinyl alcohol for deposited Ni.

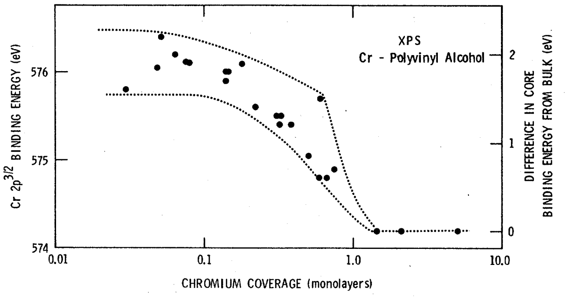

FIG. 5. Variation in the $2p^{3/2}$ electron core binding energy as a function of metal coverage on polyvinyl alcohol for deposited Cr.

value was obtained. Fourth, the largest difference in the $2p^{3/2}$ core binding energy from the bulk value for Cr and Ni on polystyrene is about 0.5 eV while for these metals on polyvinyl alcohol it is as large as 2.2 eV.

The half widths of the core levels can be extracted from the same data which produced the peak positions. Figure 6 shows the full width at half maximum (FWHM) of the $2p^{3/2}$ core levels as a function of metal coverage for the systems studied. No attempt was made to extract the instrument response function. The lines through the data are simply for an aid to the eye. For Cu on polystyrene, the Cu core levels having a binding energy less than the bulk value, Fig. 1, also have an FWHM of ~1.7 eV, less than the measured FWHM for bulk Cu. It should also be noted that when the metals are deposited on polyvinyl alcohol, the FWHM are greater than those for metals on polystyrene (for coverages less than a monolayer or so). Finally, for Cr on polystyrene, as the Cr coverage decreases below ~0.5 monolayer, the FWHM also decreases.

In addition to the information obtained from the core line shapes of the overlayer atoms, we can learn more about the interface reactions by examining the line shapes of the substrate polymer atoms. For Cu, Ni, and Cr deposited on polystyrene, there were no measurable changes in the C1*s* core level except for a decrease in intensity caused by overlayer attenuation. However, the addition of these metal atoms to the surface of the polyvinyl alcohol modifies the line shapes of the core levels of the surface carbon and oxygen atoms.

On the clean polyvinyl-alcohol surface, the C1*s* core line shape consists of a single broad peak centered at 285.8 eV and the O1*s* line shape of a single narrow peak at 532.9 eV binding energy. The carbon line can be deconvolved into two components,[22] one with a peak at 285.0 eV associated with a CH_2 group and one with a peak at 286.6 eV associated with an HCOH group. After Cu, Ni, or Cr atoms were deposited, the overall intensity decreased and the line shape altered. The line shape changes can best be shown by difference curves. To account for the simple attenuation of the metal overlayer, the 285.0 eV component of the C1*s* and the 532.9 eV component of the O1*s* line were normalized before and after deposition of the metal overlayer. The resulting difference curve is then a measure of the chemical changes taking place on the surface. Figures 7 and 8 show the normalized line shapes and their difference curves for the C1*s* and O1*s* core levels, respectively, following deposition of ~0.6 monolayer of Cu on polyvinyl alcohol. Figure 9 shows the same difference curves following deposition of 0.33 monolayer of Ni on polyvinyl alcohol and Fig. 10 shows the difference curves following deposition of 0.33 monolayer of Cr on polyvinyl alcohol. The noise level in the individual core spectra were in general 10 counts/sec or less. Thus we regard only structure in the difference curves of more than 50 counts/sec as being indicative of a change.

Overall, these difference curves are very similar for the three different metals. Each produces a relative decrease in the C1*s* signal at 286.6 eV and each causes new structures to appear at lower binding energy in the O1*s* spectrum. With the addition of copper, this new peak is at 530.6 eV, at 531.6 eV with nickel, and at 531.2 eV with the addition of chromium to the polyvinyl-alcohol surface. The energy positions of these changes were independent (±0.1 eV) of the amount of metal adsorbed. The signal in Fig. 9(b) for binding en-

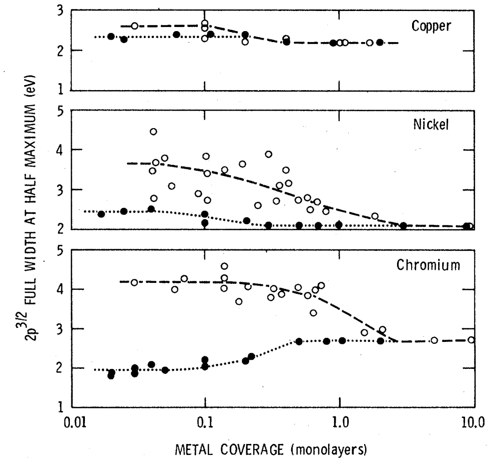

FIG. 6. Variation in the FWHM of the $2p^{3/2}$ electron core levels as a function of metal coverage on polystyrene (full circles) and on polyvinyl alcohol (open circles) for deposited Cu, Ni, and Cr.

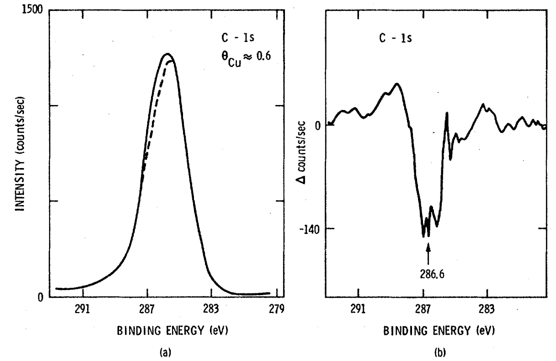

FIG. 7. (a) Carbon-1*s* spectrum of a clean (solid curve) and a copper-covered (dotted curve) polyvinyl-alcohol surface. (b) Difference spectrum in the carbon-1*s* energy region between a copper-covered and a clean polyvinyl-alcohol surface. The copper coverage θ_{Cu} is 0.6 monolayer.

ergies greater than 534 eV is part of a nickel Auger peak.

IV. DISCUSSION

After a careful analysis of the data, it is clear that the substrate plays a major role in determining the properties of the metal overlayer. This is not entirely surprising in light of previous work using metal and semiconductor substrates. However, the relatively large changes in the data occurred by simply replacing a C_6H_5 group with an OH group on a polymer backbone. It is just this OH group that causes the peak position and FWHM of the $2p^{3/2}$ line shapes to vary so differently as a function of metal coverage when we compare the polyvinyl-alcohol data to the polystyrene data. When a metal atom first bonds to a polyvinyl-alcohol surface, it is able to bond rather strongly with an oxygen atom already present, forming a metal-oxygen-polymer complex.[6] This changes both the initial electronic state of the metal atom as well as the atomic and extra-atomic screening contributions to the measured photoemission energy.

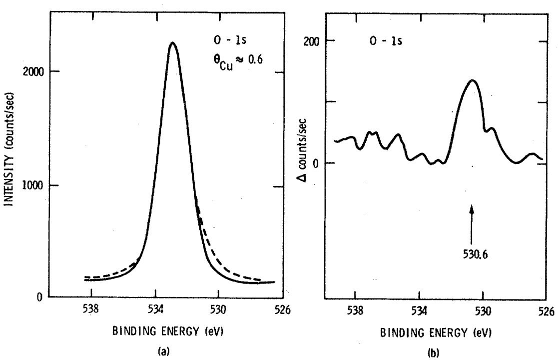

FIG. 8. (a) Oxygen-1*s* spectrum of a clean (solid curve) and a copper-covered (dotted curve) polyvinyl-alcohol surface. (b) Difference spectrum in the oxygen-1*s* energy region between a copper-covered and a clean polyvinyl-alcohol surface. The copper coverage θ_{Cu} is 0.6 monolayer.

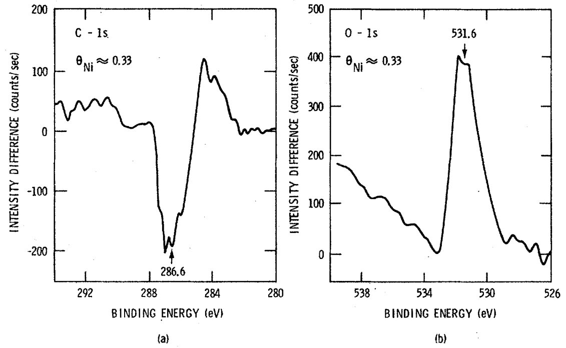

FIG. 9. (a) Difference spectrum in the carbon-1*s* energy region between a nickel-covered and a clean polyvinyl-alcohol surface. (b) Difference spectrum in the oxygen-1*s* energy region between a nickel-covered and a clean polyvinyl-alcohol surface. The nickel coverage θ_{Ni} is 0.33 monolayer.

It has previously been pointed out[8,9,11,12,15] that changes in screening can account for the general changes in binding energy as a function of coverage such are as observed in Figs. 1–5. In particular, we have discussed[15] the results for Cu on polystyrene and have indicated that changes in screening as the particle-size changes can account for the upper curve in Fig. 1. On the other hand, the state of Cu with a binding energy less than the bulk was attributed[15] to a state in which both the screening as well as the initial electronic state of Cu was changed, relative to the bulk. The differences between Cu, Ni, and Cr on polystyrene can be attributed[23] to differences in the mobilities

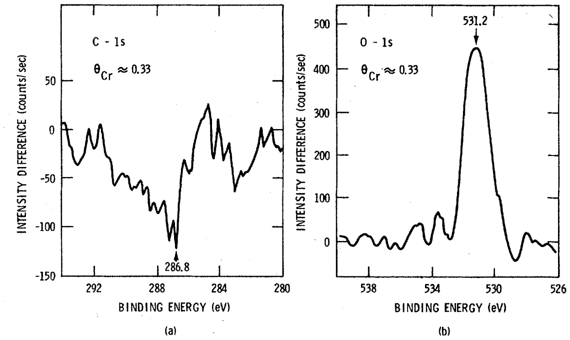

FIG. 10. (a) Difference spectrum in the carbon-1*s* energy region between a chromium-covered and a clean polyvinyl-alcohol surface. (b) Difference spectrum in the oxygen-1*s* energy region between a chromium-covered and a clean polyvinyl-alcohol surface. The chromium coverage θ_{Cr} is 0.33 monolayer.

of the metal atoms. Both the Ni and Cr $2p^{3/2}$ core levels reach the bulk value before one monolayer, indicating that they form larger clusters with bulk screening values more rapidly than does Cu. But when these metals are deposited on polyvinyl alcohol, the shapes of the curves, Fig. 2, change dramatically, Figs. 4 and 5. In addition, the FWHM for Ni and Cr also change. This indicates a rather different state for the metal atoms on the surface in which the initial state and/or atomic and extra-atomic screening is different.

We can obtain another clue to the makeup of this new state by examing the changes in the substrate core line shapes, Figs. 7–10. The difference curves indicate that the metal atoms have perturbed the original C-O bonds and formed (partial) bonds with the oxygens. The relative intensity of the change is a measure of the strength of the new bonds. The copper produces the smallest change in both the carbon and oxygen spectra (note that the Cu coverage is almost twice as large as that for Ni and Cr). This is not unexpected, as copper does not react as strongly with oxygen as do nickel and chromium.[24-27] The initial sticking coefficient of oxygen on Cu is lower than it is on Cr or Ni and the dissociation energy of copper oxide is much lower than that of chromium or nickel oxide. For all three metals, the additional structure in the O1*s* spectrum lies between the polyvinyl-alcohol binding energy and the appropriate bulk-metal–oxide binding energy[24-26] or the binding energy for chemisorbed oxygen.[25-27] This implies that the oxygen is still partially bonded to the polymer and indeed a metal-polymer complex has been formed at the interface. Unfortunately, the exact configuration of this complex cannot be deduced from the energy values of the XPS structure. There is simply not enough information. However, it is possible that a vibrational spectroscopy such as infrared, Raman, or electron energy loss would yield the molecular configuration of such a polymer-metal complex.

The existence of these metal-oxygen-carbon complexes can account for many of the observed changes already discussed. We expect the metal to be more tightly bonded to the polymer polyvinyl alcohol through such a complex than if one was not present, as on clean polystyrene. Indeed, semiquantitative adhesion results confirm this: Copper, nickel, and chromium adhere better to polyvinyl alcohol than to clean polystyrene and better to oxygen-treated polystyrene than to clean polystyrene.[6] A stronger bond between the metal and the polymer would reduce the migration of metal atoms on the surface. This means smaller clusters would be formed at any given coverage, implying smaller relaxation energies and a resulting larger shift in core binding energy from the bulk value, as evidenced in Figs. 3–5. This would also account for the larger scatter in the data on polyvinyl alcohol, for the metal atoms would tend to stay near where they first contacted the surface. Thus a series of different depositions on polyvinyl alcohol could easily give a series of different results. However, on polystyrene where the binding of the metal atoms is relatively weak, the memory of the arrival site tends to be erased.

This effect should also be seen in the FWHM data. If we examine the data, Fig. 6, we see for coverages less than a monolayer that the metal FWHM is larger on polyvinyl alcohol than on polystyrene. The FWHM also increases as the metal coverage decreases below one monolayer for copper and nickel on polyvinyl alcohol and polystyrene and for chromium on polyvinyl alcohol. This increase in the FWHM can be explained by a combination of two effects: a change in the atomic and/or extra-atomic screening and an inhomogeneous distribution of particle sizes. Ascarelli *et al.*[8] have pointed out that if the screening in a small particle is reduced, then the measured XPS line widths will increase. In our case, we know the screening of the metal atoms was reduced because the electronic core binding energies were increased above the bulk values. On the other hand, the scatter in the core energy data for metals on polyvinyl alcohol indicates a rather inhomogeneous distribution of particle sizes. A distribution of particle sizes (at any one coverage) would imply a distribution of metal core binding energy values which would result in a measured core line shape having a larger FWHM.

Throughout this discussion, we have not said anything about the anomaly in the FWHM data for Cr on polystyrene. For this system, as the Cr coverage decreases, the FWHM also decreases. This is also opposite in direction from that caused by reduced screening (according to Ref. 8) and opposite to all other systems for which FWHM data have been reported[7-9,13,28] as a function of coverage. Note that for Cu on polystyrene, the state of Cu having a $2p^{3/2}$ core electron binding energy 1.5 eV less than the bulk value also has a $2p^{3/2}$ core FWHM which is less than the bulk value. Obviously, there are factors other than screening or particle-size distribution which have a measurable effect on the FWHM. It is hoped that future work on other systems will help us find them.

ACKNOWLEDGMENTS

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[1] K. L. Mittal, J. Vac. Sci. Technol. 13, 19 (1976) and references therein.

[2] D. W. Thayer and R. Wedel (unpublished).

[3] J. R. Hall, C. A. Westerduhl, A. T. Devine, and M. J. Bodnar, J. Appl. Polym. Sci. 13, 2085 (1969).

[4] J. R. Hall, C. A. Westerduhl, A. T. Devine, and M. J. Bodnar, J. Appl. Polym. Sci. 16, 1465 (1972).

[5] J. M. Burkstrand, J. Vac. Sci. Technol. 15, 223 (1978).

[6] J. M. Burkstrand, Appl. Phys. Lett. 33, 387 (1978).

[7] K. S. Liang, W. R. Salaneck, and I. A. Aksay, Solid State Commun. 19, 329 (1976).

[8] P. Ascarelli, M. Cini, G. Missoni, and N. Nistico, J. Phys. (Paris) Colloq. 38, 125 (1977).

[9] Y. Takasu, R. Unwin, B. Tesche, A. Bradshaw, and M. Grunze, Surf. Sci. 77, 219 (1978).

[10] G. G. Tibbetts and W. F. Egelhoff, Jr., Phys. Rev. Lett. 41, 188 (1978).

[11] G. G. Tibbetts and W. F. Egelhoff, Jr., J. Vac. Sci. Technol. 16, 661 (1979); Solid State Commun. 29, 53 (1979); Phys. Rev. B 19, 5028 (1979).

[12] M. G. Mason, L. G. Gerenser, and S. T. Lee, Phys. Rev. Lett. 39, 288 (1977).

[13] K. S. Kim and N. Winograd, Chem. Phys. Lett. 30, 91 (1975).

[14] M. G. Mason and R. C. Baetzold, J. Chem. Phys. 64, 271 (1976).

[15] J. M. Burkstrand, J. Vac. Sci. Technol. 15, 658 (1978); Surf. Sci. 78, 513 (1978).

[16] Physical Electronics Industries, Eden Prairie, Minn.

[17] J. H. Scofield, Lawrence Livermore Laboratory Report No. UCRL 51326 (unpublished).

[18] J. C. Tracy and J. M. Burkstrand, CRC Crit. Rev. Solid State Sci. 4, 381 (1974).

[19] S. Evans *et al.*, J. Phys. C 10, 2483 (1977).

[20] See for example: A. Joshi, L. E. Davis, and P. W. Palmberg, in *Methods of Surface Analysis*, edited by A. W. Czanderna (Elsevier, Amsterdam, 1975), p. 159.

[21] D. T. Clark and H. R. Thomas, J. Polym. Sci., Polym. Chem. Ed. 14, 1671 (1976).

[22] This is consistent both with the work of Ref. 24 and with D. T. Clark and H. R. Thomas, J. Polym. Sci., Polym. Chem. Ed. 16, 791 (1978).

[23] J. M. Burkstrand, J. Appl. Phys. 50, 1152 (1979).

[24] J. Haber, T. Machej, L. Ungier, and J. Ziolkowski, J. Solid State Chem. 25, 207 (1978).

[25] T. Fleisch, N. Winograd, and W. Delgass, Surf. Sci. 78, 141 (1978).

[26] G. C. Allen, P. M. Tucker, and R. K. Wild, Faraday Trans. II, 74, 1126 (1978).

[27] G. G. Tibbetts, J. M. Burkstrand, and J. C. Tracy, Phys. Rev. B 15, 3652 (1977).

[28] G. G. Tibbetts and W. F. Egelhoff (private communication, data from Ref. 11).