PHYSICAL REVIEW B VOLUME 36, NUMBER 3 15 JULY 1987-II

Schottky-barrier formation on a covalent semiconductor without Fermi-level pinning: The metal-$MoS_2(0001)$ interface

Jeffrey R. Lince, David J. Carré, and Paul D. Fleischauer
Chemistry and Physics Laboratory, The Aerospace Corporation, El Segundo, California 90245

(Received 5 January 1987)

Chemical interaction and Schottky-barrier formation at the metal-MoS_2 interface were studied by evaporating metals (Ag, Al, Au, Co, Fe, In, Mn, Pd, Rh, Ti, and V) onto the (0001) basal-plane surface of cleaved molybdenite, and then analyzing the interface with x-ray photoelectron spectroscopy (XPS). Except for Mn, negligible changes were revealed in the Mo ($3d_{5/2}$) and S ($2p_{3/2}$) peak shapes, or widths, after deposition. The shifts in the binding energies did not correlate with the electron configuration of the metal but rather with the metal electronegativity, and are interpreted in terms of band bending at the metal-semiconductor interface, rather than chemical reaction. Plots of both Mo and S binding energies versus metal electronegativity yield approximately linear curves with nonzero (positive) slopes, which provide an average "index of interface behavior" of $S'=1.28\pm0.22$. This value is considerably higher than for other covalent semiconductors, which exhibit $S'<0.3$ due to Fermi-level pinning. The anomalous behavior of MoS_2 results from the extreme inertness of the basal-plane surface and the stability of the layered crystal lattice of MoS_2. The absence of chemical interaction at the interface causes the formation of a Schottky barrier exhibiting behavior that may approach the Schottky limit. This behavior for $MoS_2(0001)$ is compared with that of other semiconductors, and is discussed in terms of their ionicity, reactivity, and dielectric response. Metals (Ag, Au, Co, Cu, Fe, Pd, Ti, and V) were also deposited onto $MoS_2(0001)$ surfaces that were bombarded with 10-keV Ar^+ ions. The Fermi level was not strongly pinned, even though defect densities as high as $\sim 3\times10^{14}$ cm^{-2} were produced in the surface region.

I. INTRODUCTION

The basic physical mechanism behind the formation of a Schottky barrier at the metal-semiconductor interface remains elusive. Various degrees of "pinning" of the Fermi level (E_F) within the band gap of the semiconductor cause metal-semiconductor contacts to deviate from the ideal "Schottky limit," where the Schottky-barrier height (ϕ_b) is given by the difference between the metal work function (ϕ_m) and the electron affinity of the semiconductor.[1] Although the pinning was originally attributed to the presence of electronic states intrinsic to the clean semiconductor surface,[2] two recent models, based on the notion that the electronic states pinning E_F are caused by the interaction of the metal with the semiconductor, have gained prominence. In one model, Spicer and co-workers[3,4] suggest that those states result from defects in the semiconductor that are produced from chemical reaction or heat of condensation as the metal is deposited from the vapor phase, giving rise to states that are extrinsic to the interface. In the other model, which was proposed by Heine[5] and later developed by Louie and co-workers[6] and by Tersoff,[7] "metal-induced gap states" (MIGS) are created by the tunneling of the wave function of the metal electrons into the semiconductor, creating states in the band gap, i.e., states that are intrinsic to the interface. Recently, other models have been proposed; for example, Ludeke and co-workers[8] have suggested that E_F can be pinned by metal-derived gap states caused by chemical interactions between the metal and the semiconductor constituents. Comparing the amount of Fermi-level pinning for semiconductors of varying physical and chemical properties can help to evaluate the applicability of these models.

The degree of Fermi-level pinning may be expressed in terms of an "index of interface behavior," $S_{WF}(=d\phi_b/d\phi_m)$, where $S_{WF}\cong0$ corresponds to strong pinning and $S_{WF}=1$ corresponds to the Schottky limit. Mead[9] has proposed that the electronegativity of the metal, χ_m, is a more appropriate reference for ϕ_b, because the work function includes a contribution from the surface dipole, which will be unpredictably altered as the metal-semiconductor interface is formed. Kurtin and co-workers[10] have examined the dependence of $S'(=d\phi_b/d\chi_m)$ on the semiconductor ionicity, as measured by the difference in the electronegativities of the constituents in the semiconductor. Their results are summarized in Fig. 1 and are characterized by values of $S'\leq0.3$ for covalent semiconductors, an abrupt "covalent-ionic" transition in S' at $\Delta\chi\cong0.7-0.8$, and a saturation at $S'\cong1$ for ionic semiconductors ($\Delta\chi=\chi_{\text{cation}}-\chi_{\text{anion}}$). Schluter[11] reevaluated the original data in Ref. 10 and has determined that there is high scatter in some of the data, and that saturation occurs not for $S'=1$, but for $S'=2.0-3.0$. The basic transition at $\Delta\chi\cong0.7-0.8$, however, is still evident (as discussed in Sec. III B).

The difference in Schottky-barrier behavior between the covalent and ionic semiconductors probably originates in the differences in their reactivities[12,13]—a reasonable assumption since most current theories on Schottky-barrier formation point to some degree of chemical bonding

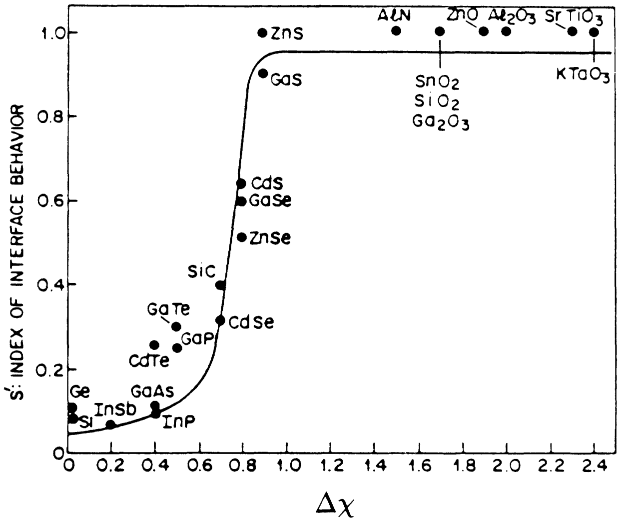

FIG. 1. Original plot from Kurtin *et al.* (Ref. 10) of the "index of interface behavior," S', vs the difference in electronegativities, ΔX, of the semiconductor constituents. The plot is characterized by $S' \lesssim 0.3$ for covalent semiconductors, a rapid increase in S' at $\Delta X \cong 0.7-0.8$ (the "covalent-ionic transition"), and a "saturation" at $S' \cong 1.0$ for ionic semiconductors. (Reprinted with permission of T. C. McGill and the American Institute of Physics.)

and/or reaction as the cause of E_F pinning in the covalent semiconductors.[3,8,14] If reactivity at the metal–covalent-semiconductor interface can be controlled, control of S' may in turn be achieved, resulting in the ability to produce tailor-made contacts with desired values of ϕ_b: To be able to control ϕ_b on covalent semiconductors, as well as on ionic semiconductors, is desirable because the covalent semiconductors generally have lower band gaps and higher electron mobilities[15] and, therefore, are more technologically useful than ionic semiconductors.

An ideal test case for determining whether an unpinned, metal–covalent-semiconductor interface can be produced is the metal-MoS_2(0001) interface. The overall covalence of MoS_2 is attested to by (1) the electronegativity difference[16] between Mo and S of $\Delta X = 0.42$, which is well below the covalent-ionic transition at $\Delta X = 0.7-0.8$, and (2) the relatively small difference between its static and optical dielectric constants, since $\epsilon_0 = \epsilon_\infty +$ (ionic contribution).[17] The reactivity at the (0001) (basal plane) surface, however, is expected to be considerably lower than for other covalent semiconductor surfaces, because of the highly anisotropic crystal structure of MoS_2. As a transition-metal dichalcogenide compound, MoS_2 has a hexagonal layered-lattice crystal structure: A layer of the system consists of a sheet of Mo atoms sandwiched between sheets of S atoms. Bonding within the layer is covalent and strong, whereas bonding between adjacent layers is the result of weak van der Waals forces. Cleavage of the crystal along the van der Waals gap to produce a basal-plane surface does not create dangling bonds with which adsorbates may react. This description is supported by molecular-orbital calculations,[18] which indicate that the S 3*p* electrons are involved in molecular orbitals with the Mo atoms and that the S 3*s* electrons are buried in an atomic orbital that has low probability of electron density above the basal plane. Those orbitals that are available for bonding are empty, antibonding orbitals whose energies are much too high to be reasonably involved.

The chemical stability of the MoS_2(0001) surface has been corroborated through experiments demonstrating that adsorption of gases on the MoS_2 basal plane does not occur in significant amounts.[19,20] If current theories of Schottky-barrier formation are correct in assuming that chemical interactions are necessary to pin E_F, then the metal-MoS_2(0001) interface should behave close to the Schottky limit. McGovern *et al.*[21] studied the metal-MoS_2(0001) interface, but their results provided evidence of neither pinning *nor* Schottky-type behavior, indicating the need for further study. Their results will be discussed in Sec. III A.

A highly sensitive technique for investigating the metal-semiconductor interface is x-ray photoelectron spectroscopy (XPS), which can measure peak shifts due to band bending for very small amounts of deposited metal (< 1 Å). The current-versus-voltage (*I-V*), capacitance-versus-voltage (*C-V*), and internal photoemission methods are generally performed on thicker films. XPS also provides a good measure of changes in covalent bonding. In MoS_2 chemical bonding and resultant detection might occur as follows. If covalent bonding between the metal and the (sulfur-terminated) basal plane were to occur through the formation of a coordinate bond involving the electrons on the basal-plane S atoms and empty *d* orbitals on the transition metals, then sensitivity to the electronic configuration of the transition metals would be expected to be manifested in changes in the S XPS binding energy and peak shape: The strongest effect is expected for the transition metal with the most empty *d* orbitals, and little or no effect (except for band bending) is expected for metals with full *d* orbitals. (The alternative, the overlap of filled metal orbitals with empty sulfur orbitals, is considered unlikely because of the energetic considerations described above.) Since the Mo atoms probably would not be involved in covalent bonding to the transition metals to the same extent as the S atoms, the primary effects on the Mo photoelectron binding energies would be those due to band bending. Because band bending complicates chemical analysis (and vice versa), an interface that is unreactive with a particular metal might be characterized by a minimal *difference* between the XPS binding-energy shifts of the two elements in the compound semiconductor, given that band bending affects the electronic energy levels of both elements equally.

The remainder of the paper is organized as follows. Details of the metal deposition and XPS analysis are given in Sec. II. The results for the metal-MoS_2 interface are presented and discussed in Sec. III A and compared with results for other semiconductors in Sec. III B; the results for metals deposited on the Ar^+-bombarded MoS_2(0001) surface are presented in Sec. III C. Conclusions are summarized in Sec. IV.

II. EXPERIMENT

Metals that were evaporated on the $MoS_2(0001)$ surface for the purpose of measuring the band bending at the metal-semiconductor interface are as follows, Au, Ti, Ag, V, Co, Rh, Pd, Al, In, Cu, Mn, and Fe. They were purchased as thin foils or flakes in $>99.9\%$ purity. In selecting them, we considered their electronic configuration, the Gibbs free energy of the reaction of the metal with MoS_2 to form a sulfide (ΔG_r), and the metal electronegativity. Those data for the metals are listed in Table I. Thermochemical values for $\Delta G_{f,298}$ of MoS_2 and the metal sulfides (used to calculate ΔG_r) are in Ref. 22, except those for Al_2S_3 and CoS, which are in Ref. 23. The free-energy change (ΔG) is the correct predictor of the spontaneity of a reaction, not the (ΔH) enthalpy change, as reported in Ref. 12. However, in solid-state reactions with no vapor evolution,[21,24] ΔH is close to ΔG because the entropy change (ΔS) is relatively small. It should be noted that the heat of alloying was not included in our thermodynamic analysis as in Ref. 21. However, data from Ref. 21 suggest that few, if any, of the metals in this study exhibit heats of alloying with Mo that are negative and large enough to affect our comparison (see Sec. III A) of expected and actual reactivity.

MoS_2 substrates were obtained from naturally occurring single crystals of molybdenite. The crystal was cleaved under a flow of dry-nitrogen gas in a glove bag attached to the sample chamber of the XPS spectrometer, along the edge of a basal plane, with an x-acto knife, and a layer of material was peeled off. Only samples that had a smooth surface over an area that was at least as large as the XPS analysis window (i.e., 15×2 mm) were used. Previous experiments in our laboratories using Auger electron spectroscopy have shown that the adsorbed oxygen concentration on a basal-plane surface prepared in this manner is negligible ($\lesssim0.01$ monolayer), even after the sample had been sitting under vacuum for several days. Microscopic examination of cleaved samples indicated that there was generally a small concentration of edge-plane steps exposed, but these were considered to be insignificant compared to the large concentration of exposed basal plane. The cleaved samples were electrically grounded through the sample holder when placed in the XPS sample chamber, which was pumped to a base pressure of $\sim3\times10^{-8}$ Torr.

XPS analysis on the resultant metal-semiconductor interface was performed using a GCA-McPherson ESCA-36 x-ray photoelectron spectrometer with a hemispherical electron energy analyzer that was modified to include optical multichannel detection,[25] which enchances data-collection speed. The excitation source was the Mg $K\alpha$ x-ray line at 1253.6 eV, and all the spectra were referenced to adventitious carbon using the C 1*s* peak, which

TABLE I. Electronic and chemical data of metals discussed in this study.

Metal	Used in Fig. 3[a]	Used in Fig. 6[b]	Electron occupancy[c]	ΔG_r[d] (kcal/mol)	Sulfide[e]	Pauling electronegativity[f]
Ag	*Y*	*Y*	$4d^{10}5s^1$	+9.6	Ag_2S	1.93
Al	*Y*		$3s^23p^1$	−43.5	Al_2S_3	1.61
Au	*Y*	*Y*	$5d^{10}6s^1$	no reaction		2.54
Co	*Y*	*Y*	$3d^74s^2$	+7.2 +22.9	CoS Co_2S_3	1.88
Cu		*Y*	$3d^{10}4s^1$	+3.2	Cu_2S	1.90
Fe	*Y*	*Y*	$3d^64s^2$	+3.0 +14.1	FeS FeS_2	1.83
In	*Y*		$5s^25p^1$	−4.5 −8.8	InS In_2S_3	1.78
Mg			$3s^1$	−54.7	MgS	1.31
Mn	*Y*		$3d^54s^2$	−25.2	MnS	1.55
Ni			$3d^84s^2$	+2.3	Ni_3S_2	1.91
Pd	*Y*	*Y*	$4d^{10}$	+2.8	Pd_4S	2.20
Rh	*Y*		$4d^85s^1$	not available		2.28
Ti	*Y*	*Y*	$3d^24s^2$	−24.1	TiS	1.54
V	*Y*	*Y*	$3d^34s^2$	−73.0	V_2S_3	1.63

[a] Metals deposited on cleaved $MoS_2(0001)$ surface.

[b] Metals deposited on $MoS_2(0001)$ surface after 10-kV Ar^+ bombardment.

[c] Occupancy of highest one or two shells.

[d] Calculated from $\Delta G_{f,298}$ values in Refs. 22 and 23 for the reaction $M+(b/2a)MoS_2\rightarrow(1/a)M_aS_b+(b/2a)$ Mo.

[e] Possible sulfide products of reaction in footnote d.

[f] From Ref. 16.

was set arbitrarily to a binding energy of 285.0 eV. Auger measurements in our laboratory have indicated that the carbon is present in amounts of <0.2 monolayers on $MoS_2(0001)$ surfaces cleaved under the conditions reported here.

Shifting of the C 1*s* peak in this study contributed partially to the shifting of the corrected binding-energy shifts. The C 1*s* shifts appeared to correlate somewhat (nonreproducibly) with the electronegativity of the deposited metal—larger shifts occurred for metals with lower electronegativity—but the C 1*s* shifts were highly inconsistent: when repeating the deposition of a particular metal on a fresh substrate, there were wide variations (>0.6 eV) in the C 1*s* binding energy. In contrast, the *corrected* Mo $3d_{5/2}$ and S $2p_{3/2}$ binding energies (see Table II) showed much less scatter than the (uncorrected) C 1*s* binding energies, and they were far more consistently correlated with the metal electronegativity. In addition, there were no changes in the C 1*s* peak shape after deposition, indicating the lack of chemical reaction with the carbon. Therefore, the use of carbon as a reference for the XPS spectra was deemed appropriate.

The Mo and S XPS spectra for freshly cleaved, single-crystal $MoS_2(0001)$ surfaces are shown in Fig. 2(a). The Mo $3d_{3/2}$ and $3d_{5/2}$ peaks are clearly resolved. The S $2p_{1/2}$ and $2p_{3/2}$ peaks are only partially resolved, owing to the low resolution of the spectrometer. The maximum of the S peak in Fig. 2(a) corresponds to the $2p_{3/2}$ peak position and will be used in the subsequent analyses. The shifts in the Mo $3d_{5/2}$ and S $2p_{3/2}$ peak binding energies were employed as a measure either of band bending or of changes in effective nuclear charge.

Metal foils were cut into strips and wrapped around the tungsten filament in the spectrometer evaporation unit (McPherson model 36-L), so that the evaporations could be performed *in situ,* without exposing the cleaved molybdenite samples to atmosphere. The chamber pressure was $<1\times10^{-7}$ Torr during the metal evaporations. During the evaporations, the XPS spectra of Mo, S, and the deposited metal were checked intermittently to verify metal deposition and to halt the deposition at a thickness that still permitted detection of the underlying S and Mo photoelectron signals. No provision was made for directly measuring the thickness of the metal layers; approximate thicknesses were calculated using the Mo $3d_{5/2}$ and/or the S $2p_{3/2}$ peak intensities before and after evaporation with the following equation:[26]

$$I=I_0\exp(-t/\lambda\cos\theta)\ ,$$

where I is the peak intensity in total photoelectron counts, λ is the photoelectron escape depth for the element, t is the evaporated metal thickness, θ is the angle between the photoelectron analyzer and the surface normal, and I_0 is a constant that is a function of the instrument and the element analyzed. I_0 was evaluated using the S or Mo peak intensity before evaporation, where $t=0$. This method is quantitative only for films with uniform thickness. In general, however, metals tend to form disconnected, three-dimensional islands on $MoS_2(0001)$.[27] Therefore, the calculated values must be assumed to represent *minimum* values for the thickness. Using this approach, minimum evaporated metal thicknesses of from ~7 to ~100 Å were calculated. Metal depositions were repeated at least twice, with some variation in thickness each time. The results of this study appeared, generally, to be independent of the metal thickness: The results for a particular metal were reproducible (within the stated error limits).

After the metal deposition, the XPS spectra were repeated over several analysis angles θ in order to attempt a qualitative determination of the distribution of species in the direction of surface normal. No reproducible correlation between peak intensity and θ was observed for Mo or S. This lack of angle dependence was attributed to small buckling ($\sim5°$) in the crystal, the presence of cleavage steps, and highly uneven metal-film morphology (island formation[27]). However, binding-energy results were reproducible over the various analysis angles, and the main results presented in this paper are dependent on binding energy rather than peak intensity.

Because of the lack of ultrahigh-vacuum conditions, some of the metals exhibited varying degrees of oxidation (i.e., oxide formation). Ti was almost completely oxidized and was not used to calculate S', as we discuss below. Mn and Al showed oxidation in the 10–50% range, depending on how long XPS analysis was delayed after metal deposition. However, the Mo and S binding energy shifts were reproducible over this entire range of oxidation levels (within the stated error limits), suggesting that as long as *some* metal existed at the metal-$MoS_2(0001)$ interface, the existence of the oxide could be neglected for Mn and Al. Of the other metals, Fe had $\lesssim20\%$ oxidation; Co, In, Pd, and V had $\lesssim5\%$ oxidation; and Ag, Au, and Cu had negligible oxide formation. Therefore, since neither the presence nor lack of oxide detected by XPS affected our analysis of S', we conclude that the effect of oxide formation on our results is negligible. One possible explanation for this lack of effect is that the ratio of the metal-oxide to metal-element XPS peak intensities increased as θ was increased, indicating that most of the oxide formed on the outer surface of the metal film, *away* from the metal-semiconductor interface. It should also be noted that at no time in this study was there evidence of a Mo VI peak, characteristic of oxidized Mo (see Fig. 2).

Metals were also deposited on Ar^+-bombarded surfaces (see Table I). The Ar^+ ions were produced from a McPherson model 36-K ion sputtering gun at an energy of 10 keV and a current density of $\sim20\ \mu A\,cm^{-2}$. Total fluences were $\sim5\times10^{15}\ cm^{-2}$. The sample chamber was fitted with the sputtering gun and the evaporation unit so that metal could be deposited on the ion-bombarded surfaces without exposure to atmosphere.

III. RESULTS AND DISCUSSION

A. Comparison of the behavior of various metals on $MoS_2(0001)$

After deposition of metals on $MoS_2(0001)$ [Figs. 2(b)–2(f)], there was no significant change in the shape or width of the Mo or S XPS peaks, and no extra peaks appeared that would result from the detection of both reacted and unreacted semiconductor components (except for Mn, to be discussed below). The binding energies (BE's) of the Mo and S peaks did shift considerably, however, as shown in Table II. Such shifts may be (erroneously) assumed to occur because of strong covalent bonding to the undisturbed sulfur-terminated basal-plane surface, although the lack of multiple Mo or S peaks precludes chemical decomposition of the substrate. Covalent bonding between the metal and the S atoms would cause a change in the S BE, as discussed in Sec. I, whereas it would barely effect the Mo BE. But, Table II indicates that the difference between the S and Mo BE shifts is essentially zero (within experimental error). Since the Mo and S core levels are affected about the same, lack of strong bonding or "chemisorption" of the metals on the $MoS_2(0001)$ surface can be inferred. The binding-energy shifts also do not correlate with a chemical property, such as the metal d-electron configuration or ΔG_r.

Therefore, the BE shifts must result from changes in the Fermi level of the semiconductor near the surface (i.e., band bending) rather than from changes in the effective nuclear charge of the substrate atoms from chemical interaction. Such changes in E_F are obviously not due to Fermi-level pinning, since E_F varies over a ~ 1.5-eV range, depending on the metal deposited.

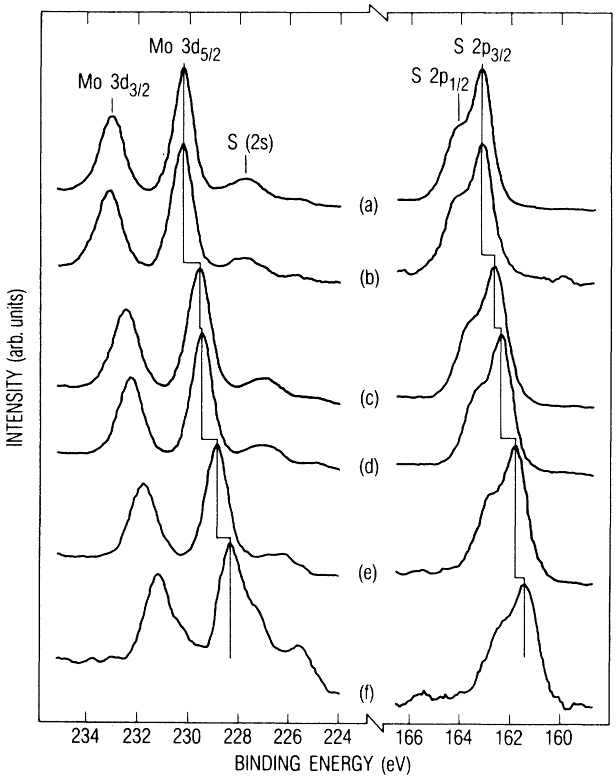

FIG. 2. X-ray photoelectron spectra of the Mo $3d$ doublet and the S $2p$ doublet of the $MoS_2(0001)$ surface (a) when freshly cleaved, and after the deposition of (b) In, (c) Pd, (d) Fe, (e) Al, and (f) Mn. Mn was the only metal in our study that showed possible evidence of chemical reaction.

To determine the index of interface behavior S', we plotted the Mo $3d_{5/2}$ and S $2p_{3/2}$ BE's against the Pauling electronegativity[16] of the deposited metals, in Figs. 3(a) and 3(b), respectively. (Some of these data were published previously.[28]) With a few exceptions (Ag and In), the data form a fairly linear plot. The data, not including these exceptions, were fitted to lines that were calculated from linear least-squares analysis. The slopes of the lines are $S'_{\mathrm{Mo}} = 1.26 \pm 0.22$ and $S'_{\mathrm{S}} = 1.30 \pm 0.19$, where the uncertainties are determined during least-square analysis. The two values are identical (within the error limits) and would therefore tend to suggest reasonable estimates of S'. For the purposes of the following discussion, the index of interface behavior is taken to be $S' = 1.28 \pm 0.22$ for metals on $MoS_2(0001)$.

Of the 11 metals in this study, eight were used to evaluate S'. The remaining three, Ag, In, and Ti, were anomalously far from the line. The XPS measurements revealed the Ti to have been almost completely oxidized to TiO_2 by the presence of background gases in the sample chamber. Therefore, it cannot be said that we produced a metal-semiconductor interface with the deposition of Ti, and the point for Ti was not shown in Fig. 3.

One possible explanation for the outlier behavior of Ag and In might be derived by comparing the behavior of several electronegativity scales as one moves from left to right along the fifth period (i.e., from Rb to Xe) in the Periodic Table. Both the Sanderson relative compactness[29] and Allred-Rochow[30] electronegativity values move fairly monotonically to higher values, whereas the Pauling values[16] move higher somewhat less monotonically and actually drop for Ag, Cd, and In before beginning to reascend. This drop probably reflects the fact that the $4d$ shell is filled for Pd, and that s and p shells are beginning to be filled for Ag, Cd, and In. Therefore, the Pauling scale may not be as appropriate in this study for Ag and In as another scale would be. In fact, when the Sanderson electronegativity values for Ag and In are used (Ag: 2.57; In: 2.86)[29] the points for Ag and In fall close to the lines in Figs. 3(a) and 3(b).

Manganese appears to be the only metal undergoing a detectable chemical reaction with MoS_2. Chemical reaction is possible, since the reaction of Mn with MoS_2 to form a sulfide is exoergic (see Table I). The Mo $3d$ doublet appears to split into four peaks with the deposition of Mn [see Fig. 2(f)]. The Mo $3d_{5/2}$ peak from MoS_2 is at ~ 228.4 eV (see Table II), whereas the second Mo $3d_{5/2}$ peak appears at ~ 1.2 eV lower BE. The lower-BE doublet appears either as a pair of very small "shoulders" on the $Mo(MoS_2)$ $3d$ doublet or as a doublet with an intensity as much as 20% that of the $Mo(MoS_2)$ $3d$ doublet, depending on the amount of Mn deposited. The logical conclusion is that Mn has reacted with MoS_2 to form a sulfide, leaving Mo metal as one of the products, given that an ~ 1.3-eV separation is expected between the Mo(metal) and $Mo(MoS_2)$ $3d_{5/2}$ peaks.[31] However, there appears to be no major change in the S $2p$ doublet, except for a small increase in peak width ($\sim 10\%$) after Mn deposition. This is not too surprising in that S tends to have an oxidation state close to (-2) even in different transition-metal chalcogenides. Although some chemical

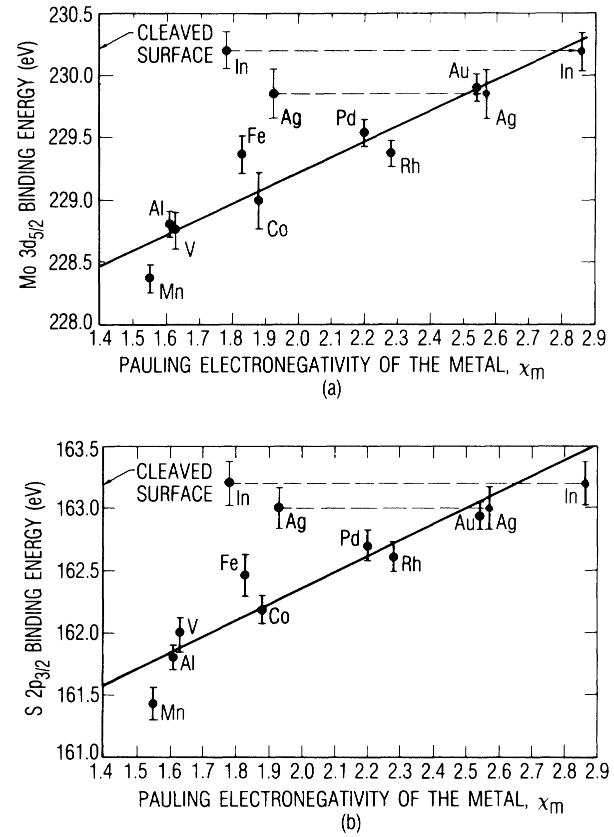

FIG. 3. Plots of the (a) Mo $3d_{5/2}$ and (b) S $2p_{3/2}$ binding energies as a function of the Pauling electronegativity of the deposited metal. Linear least-squares lines were fit to the data in both (a) and (b); their slopes are (a) $S'_{\mathrm{Mo}} = 1.26 \pm 0.22$ and (b) $S'_{\mathrm{S}} = 1.30 \pm 0.19$. The values for Ag and In were not used to calculate S', because they deviated significantly from the lines. The binding-energy values for Ag and In are also plotted as functions of Sanderson electronegativities (shaded points); these points fall much closer to the lines.

reaction occurs after Mn deposition, it must be emphasized that it does not affect the analysis of S', since both the S and Mo(MoS_2) peaks shift virtually by the same amount (see Table II). Therefore, all metals in this study appear to produce an unpinned interface, giving rise to Schottky barriers that correlate with electronegativity, independent of their expected or actual reactivity with respect to the MoS_2(0001) substrate.

Our results may now be correlated with the results of McGovern and co-workers.[21] In our experiment, we repeated deposition onto MoS_2(0001) of three of the five metals investigated by McGovern *et al.*: Al, In, and Ti. Their XPS results on Ti deposition are probably more valid than ours because they had a lower base pressure ($\sim 2 \times 10^{-9}$ Torr), which contributes to lowered oxide formation. They observed strong evidence for chemical reaction of the Ti with the MoS_2(0001) surface, but they also found a relatively large band-bending shift of ~ 1.3 eV in both the S $2p$ and Mo $3d$ peaks. When this value is plotted in Figs. 3(a) and 3(b), the resulting points fall quite close to the lines. Their value for In band bending agrees well with ours (~ 0.0 eV), as does their observation that In does not react with MoS_2(0001). As in our study, Al was found not to react with MoS_2(0001), but their band-bending values of 0.1 and 0.3 eV are considerably smaller than ours (~ 1.5 eV). The major difference between their study conditions and ours is the thickness of the Al film deposited. In their study, ~ 14 Å of Al were deposited; in ours, thicknesses of ~ 30 Å and ~ 80 Å were calculated from changes in the S and Mo peak intensities for two separate depositions (that yielded the same binding energies). That calculation, however, was shown in Sec. II to yield only minimum values for the equivalent thickness. Since metals tend to form islands on MoS_2, the actual equivalent thicknesses of Al in our study may actually be much higher than 30 or 80 Å. Therefore, for the Al interface with this nonpinned semiconductor, the thickness of Al required for stabilization of E_F may be higher than the ~ 14 Å used in the study by McGovern *et al.*

TABLE II. Binding energies of Mo $3d_{5/2}$ and S $2p_{3/2}$. Photoelectron binding energies are referenced to adventitious carbon set arbitrarily to 285.0 eV.

Metal	Mo $3d_{5/2}$ (eV)	S $2p_{3/2}$ (eV)	$\Delta E_{\mathrm{S}} - \Delta E_{\mathrm{Mo}}$ (eV)[a]
Ag	229.85±0.19	163.00±0.14	+0.11
Al	228.79±0.11	161.80±0.10	−0.03
Au	229.89±0.11	162.94±0.11	+0.01
Co	228.98±0.23	162.18±0.11	+0.16
Fe	229.36±0.14	162.46±0.15	+0.06
In	230.19±0.15	163.20±0.15	−0.03
Mn	228.37±0.12	161.43±0.13	+0.02
Pd	229.54±0.10	162.70±0.12	+0.12
Rh	229.37±0.10	162.61±0.11	+0.20
Ti (oxide)	229.30±0.20	162.53±0.15	+0.19
V	228.75±0.14	161.98±0.12	+0.19
Uncoated crystal	230.22±0.06	163.26±0.05	0
Average			0.09±0.09

[a] Difference between the S $2p_{3/2}$ and the Mo $3d_{5/2}$ binding-energy shifts with respect to the clean crystal [e.g., for V, $\Delta E_{\mathrm{S}} - \Delta E_{\mathrm{Mo}} = (161.98 - 163.26) - (228.75 - 230.22) = +0.19$].

The band-bending shift of Ni (~ 1.0 eV) that McGovern *et al.*[21] have determined appears to correlate well with electronegativity ($\chi = 1.9$) (Ref. 16) and falls close to the lines in the figures. Mg, however, exhibited a band-bending shift (~ 0.2) that is considerably smaller than the shift of ~ 1.9 eV that would be expected for Mg ($\chi = 1.3$).[16] One possible explanation for the discrepancy is, again, that the amount of deposited metal was too small (i.e., 7 Å Mg) to allow for complete E_F stabilization for this unpinned semiconductor, either because the metal layer was too thin or the surface area covered by the metal islands was too small. The fact that both Mg and Al, in the study by McGovern *et al.*, promoted E_F shifts that were considerably smaller than would be expected based on our analysis, may be the results of the relatively low electronegativities of those metals. It may be necessary to deposit them in larger thicknesses to stabilize E_F, because more electrons are transferred from the less electronegative metals during the band-bending process. Thickness, however, does not explain why Ti *does* exhibit the expected shift; they deposited only 5 Å of Ti. Obviously, the dependence of the metal-MoS$_2$ Schottky-barrier height on thickness needs to be investigated further.

It is not surprising that Ti, Mn, and Mg show evidence of reactivity with MoS$_2$, since they have negative values of ΔG_r (see Table I). What is surprising is that Al, V, and In did not indicate similar evidence of reactivity, especially since both Al and V have values of ΔG_r that are considerably more negative than for Ti. Although other metals studied had positive ΔG_r values, many had magnitudes smaller than the $\sim +11$ kcal/mol that has been hypothesized as a threshold for interface reaction at the metal-semiconductor interface.[32,33] Of the four metals, Ag, Co, Fe, and Pd, none evidenced chemical reaction. Therefore, there must be large kinetic barriers to reaction in the metal-MoS$_2$(0001) system, and those barriers are probably created by the layered structure of the MoS$_2$ crystal lattice, as discussed in Sec. I. These kinetic barriers are unique to the metal–layered-semiconductor interface, and are not necessarily expected to be present for other semiconductors.

B. Ionicity and reactivity: comparison of MoS$_2$ with other semiconductors

In Fig. 4 we have plotted the S' value for MoS$_2$ as a function of the MoS$_2$ $\Delta\chi$ value ($\chi_S - \chi_{Mo} = 2.58 - 2.16 = 0.42$),[16] together with the reevaluated S'-versus-$\Delta\chi$ data of Schluter,[11] using revised electronegativity values[16] and adding newer data points.[34,35] [The data point for SrTiO$_3$ (Ref. 11) was not included because of the difficulty of defining $\Delta\chi$ for a ternary compound.] There is considerable scatter in the data for $\Delta\chi \gtrsim 1.0$, and there is comparatively little scatter for $\Delta\chi \lesssim 0.7$: For the covalent semiconductors, S' appears to be consistently $\lesssim 0.3$. The value of $S' \cong 1.3$ for MoS$_2$ is, therefore, greater than 4 times that for the expected maximum value for a covalent semiconductor. This anomalously large value may, in fact, be close to the Schottky limit, which Cohen[36] has determined, using a static dipole model of the Schottky barrier,[37] to be ~ 1.5, rather than the 2.0–3.0 suggested by Schluter. Pong and Paudyal[34] recently demonstrated experimentally that the S' values for BaF$_2$ and LiF, two highly ionic compounds, were $\cong 1.5$ within experimental error, confirming that value.

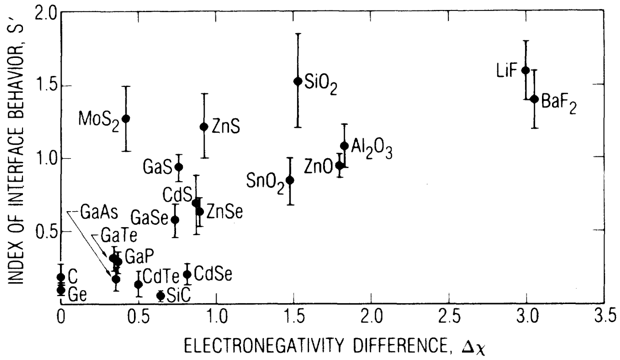

FIG. 4. Plot of S' as a function of $\Delta\chi$ data for various semiconductors in which the data from Ref. 10 (see Fig. 1) were reexamined and correlated with more recent data, including more recent electronegativity values (Ref 16). The S' values were taken from Ref. 34 (BaF$_2$ and LiF), Ref. 35 (SiC), and Ref. 11 (all the others). The value for MoS$_2$ ($S' = 1.28 \pm 0.22$) has been added to the data base; it is anomalously high for a covalent semiconductor.

Recently, an investigation similar to the present study was performed by Hughes and co-workers[33] on Schottky barriers formed by the deposition of metals on GaSe(0001), a semiconductor with a structure similar to MoS$_2$. It is a hexagonal, layered semiconductor that will cleave along a van der Waals gap without breaking covalent bonds. Its $\Delta\chi$ value is 0.74, which places it directly on the ionic-covalent transition in Fig. 4. Actually, GaSe exhibited dual behavior depending on the reactivity of the particular metal deposited. When the enthalpy of the reaction of a particular metal with GaSe to form the metal selenide was such that $\Delta H_r \lesssim +11$ kcal/[mol (metal atom)], Hughes *et al.* found that reaction proceeded and E_F was pinned ~ 0.2 eV above the flat-band location (i.e., for In, Al, Cu, and Ni). For Ag, Sn, and Au, however, no reaction occurred, and the resultant interfaces were unpinned. On the basis of the latter three metals, they calculated that $S_{\mathrm{WF}} \cong 1.4$ and that $S' \cong 2.4$, depending on whether ϕ_m or χ_m was used on the abscissa. These anomalously large values cannot be considered quantitative, because only three metals were used and because earlier data for 12 metals on GaSe gave $S' \cong 0.6$.[38]

Although both GaSe and MoS$_2$ are semiconductors that have similar layered structures, their reactivities with respect to metals deposited on their basal-plane surfaces are quite different, and are the opposite of what might be expected. Most of the values of ΔG_r for metals on GaSe are positive, but considerable reactivity and some E_F pinning has been reported. Many of the values of ΔG_r for metals on MoS$_2$ are either negative or very small and positive, but there is little reactivity (and no E_F pinning). However, MoS$_2$ appears to operate close to the Schottky limit more consistently than GaSe. The basal-plane surfaces of both GaSe and MoS_2 have no dangling bonds or surface states, so further study is required to explain this discrepancy.

An interpretation of S' in terms of the dielectric response of the metal-semiconductor system has recently been proposed by Tersoff.[14] He suggested that an increase in the metal electronegativity ($d\chi_m$) may be viewed as an increased attractive potential in the metal. This essentially gives rise to a sheet dipole at the interface. The dielectric constant ϵ is defined as the ratio of the applied potential to the effective (actual) potential in a medium.[39] The differential $d\chi_m$ may be thought of as the change in the applied potential; $d\phi_b$ would be the change in the effective potential. If we define $\bar{S} \equiv S'/A$ ($A \cong 2.8$ eV; converts Pauling electronegativity units into energy units[11]), then $\bar{S}$ is the degree to which the dipole is screened. No screening, i.e., $\bar{S}=0$, would result in the dipole's occurring within the metal; if the dipole fell completely within the semiconductor, then $\bar{S}=\epsilon_\infty^{-1}$, where ϵ_∞ is the optical dielectric constant. (The optical dielectric constant ϵ_∞ is used because the static dielectric constant ϵ_0 includes an ionic contribution: the ions are not affected by the dipole as strongly as are the electrons.[14])

Tersoff argues that, for an interface with good metal-semiconductor bonding, the screening will be a monotonic function of dipole position, i.e., $0 \leq \bar{S} \leq \epsilon_\infty^{-1}$. The S' values in Fig. 4 were converted to $\bar{S}$ and plotted against ϵ_∞^{-1} (as in Ref. 14) in Fig. 5. Only data for which reliable ϵ_∞ data were available[14,40] were used. The data for semiconductors with strong pinning ($\bar{S} \leq 0.07$) fall near a line represented by $\bar{S}=\frac{1}{2}\epsilon_\infty^{-1}$, implying that the dipole occurs at the interface (i.e., neither completely in the metal nor in the semiconductor)—a relationship that argues for a Fermi-level-pinning mechanism involving electronic states that are intrinsic to the metal-semiconductor interface.[14] For semiconductors that show only weak pinning ($\bar{S} > 0.1$), the data appear near or above the upper bound ($\bar{S}=\epsilon_\infty^{-1}$). Violation of that upper bound indicates a breakdown in the assumption of a smooth variation of the dielectric response across the interface, a breakdown that Tersoff proposes is caused by poor interfacial bonding between the metal and the less reactive, ionic semiconductors.

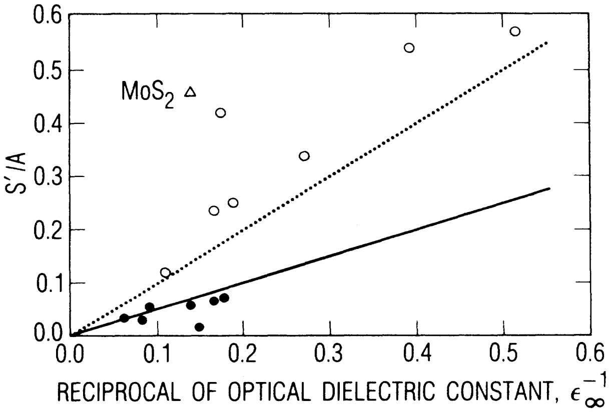

FIG. 5. Plot of $\bar{S}$ ($=S'/A$, where $A \cong 2.8$) vs ϵ_∞^{-1} [originally plotted in Ref. 14 and supplemented here with additional S' data and additional dielectric constant data (Ref. 40)]. Solid line is $\bar{S}=\frac{1}{2}\epsilon_\infty^{-1}$, and dotted line is upper bound, $\bar{S}=\epsilon_\infty^{-1}$. Solid circles represent semiconductors with strong pinning ($\bar{S} \lesssim 0.07$); open circles represent weaker pinning ($\bar{S} > 0.1$). (Solid circles are, from left to right, Ge, Si, GaAs, CdTe, SiC, CdSe, C; open circles are GaP, ZnSe, ZnS, CdS, ZnO, SiO_2, LiF.) The data point for MoS_2 has been added to the figure (triangle). Its $\bar{S}$ value is over 3 times greater that the upper bound, indicating lack of a smooth variation of the dielectric response across the interface because of poor interfacial bonding.

When the data point for MoS_2 is plotted in Fig. 5 (ϵ_∞ from Ref. 17), $\bar{S}$ is over 3 times higher than the line signifying the upper bound. The extreme inertness of the $MoS_2(0001)$ surface probably causes the formation of a highly abrupt interface with poor interfacial bonding, corroborating Tersoff's argument about the lack of chemical reactivity at unpinned metal-semiconductor interfaces.

From the dependence of most Schottky-barrier theories on the chemical behavior of the interface, one can infer that S' is a function mainly of the metal-semiconductor interfacial chemistry. The behavior of S' with respect to semiconductor ionicity probably occurs only because ionicity is strongly correlated with reactivity (as discussed in Sec. I). That this relationship exists points to the use of an index describing the reactivity of the semiconductor in order to predict Schottky-barrier behavior. The use of ΔH (or more accurately ΔG) as that index is appropriate only for equilibrium situations. The anomalously high S' value for $MoS_2(0001)$ indicates that orientation and surface structure are also important, since they may create a barrier to solid-state reaction. Therefore, kinetics and thermodynamic considerations should be taken into account when attempting to predict Schottky-barrier behavior. In cases for which there is no significant kinetic barrier to reaction, ionicity or ΔG_f (semiconductor) might be an appropriate index to describe Schottky-barrier behavior.

C. Metals on ion-bombarded MoS_2

To investigate the possibility of increasing the reactivity of the basal-plane surface of MoS_2, cleaved $MoS_2(0001)$ surfaces were bombarded with 10-keV Ar^+ ions (total fluence approximately equal to 5×10^{15} cm^{-2}) prior to metal deposition. Detailed studies in our laboratory[28,41] have used XPS and Auger electron spectroscopy to demonstrate that the surface region (~30 Å detection depth) is depleted significantly of S after ion bombardment (IB) with Ar^+ under these conditions (i.e., if R is defined as S-Mo XPS peak area ratio, then with IB, $\Delta R/R \cong -15\%$). In addition, band-bending shifts were indicative of a small amount of metallic Mo forming on the Ar^+-bombarded $MoS_2(0001)$ surface.

Plots of Mo and S binding energies, similar to Figs. 3(a) and 3(b), are shown in Figs. 6(a) and 6(b). There is far more uncertainty in the values for the individual data points than in Fig. 3, and there is also somewhat greater scatter of the data points about the least-squares lines fitted to them, complicating an evaluation of S'. Although quantitative analysis is difficult, the average value for S' of 0.6 ± 0.2 implies that there is only weak pinning of E_F after IB, which is surprising, because a change in the S-Mo ratio of 15% suggests a defect density of *at least* 4×10^{14} cm^{-2} within the XPS detection volume. According to Zur and co-workers,[42] the defect density required to pin E_F would be 10^{12} and 10^{14} cm^{-2} for submonolayer and thick films of metal, respectively; hence, ion bombardment in this study should be adequate to pin E_F. Therefore, it appears that the "unified defect model" of Spicer *et al.*[3,4] is not applicable *in this case*. This conclusion is not necessarily applicable to their model for III-V compound semiconductors: Although they have similar ionicities, MoS$_2$ and the III-V compounds have very different electronic properties and crystal structures, and would therefore have different defect properties.

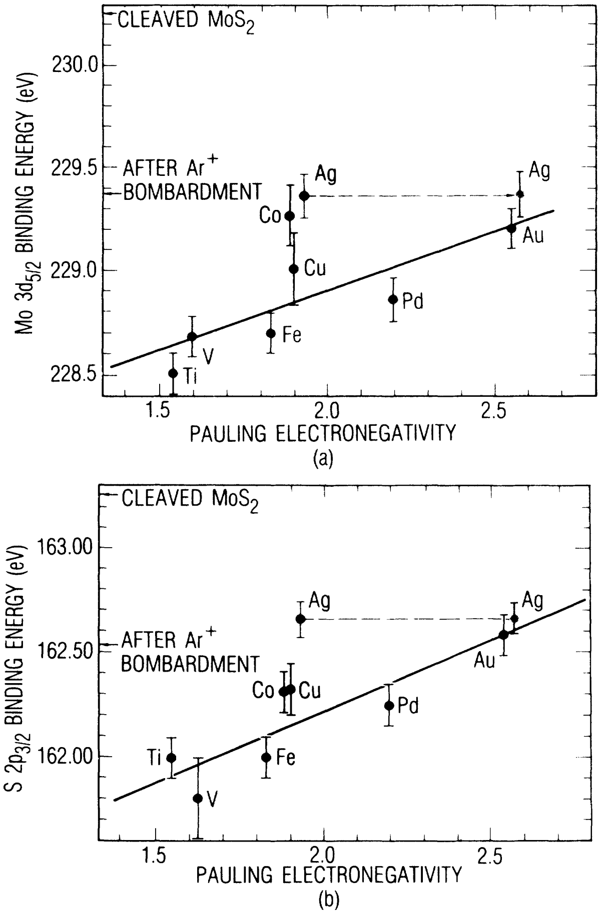

FIG. 6. Plots similar to Fig. 3, except that MoS$_2$ surfaces were subjected to 10-keV Ar$^+$ bombardment ($\sim5\times10^{15}$ cm^{-2}) prior to metal deposition, for (a) Mo $3d_{5/2}$ binding energy, and (b) S $2p_{3/2}$ binding energy. The slopes in the lines were calculated to be (a) $S'_{\mathrm{Mo}}=0.59\pm0.16$ (excluding the data point for Co) and (b) $S'_{\mathrm{S}}=0.67\pm0.18$. The binding-energy value for Ag is also plotted as a function of the Sanderson electronegativity of Ag, similar to Fig. 3.

The ability of MoS$_2$ to avoid pinning, even under such large defect densities, might be related to the stability of its lattice as changes occur in stoichiometry. A recent study by Dimigen and co-workers[43] illustrates this phenomenon. They investigated the crystallinity of rf-diode-sputtered MoS$_x$ films and observed that the crystallites in the films maintained the $2H$-MoS$_2$ structure to values as low as $x\cong1.0$. Since, in our study, the concentration at the surface is probably $x\cong1.7$ after IB, the basic crystalline structure of the first few molecular layers may be intact, preserving the ability of MoS$_2$ to avoid pinning.

Although no strong pinning has been revealed for metals on the Ar$^+$-bombarded MoS$_2$(0001) surface, chemical reaction or strong covalent bonding may be manifested by the unequal movements of the S $2p_{3/2}$ and Mo $3d_{5/2}$ binding energies when either Ti or Co is deposited. The Ti deposited after IB showed only partial oxidation, explaining its proximity to the least-squares lines as contrasted to nonbombarded surfaces, in which almost complete oxidation of the Ti had occurred.

IV. CONCLUSIONS

We have investigated the chemistry and band-bending behavior of the metal-semiconductor interface formed by the evaporation of metals of varying electronic orbital occupation, reactivity, and electronegativity on cleaved MoS$_2$(0001) surfaces. X-ray photoelectron spectroscopy revealed no evidence of chemical reaction between the metals and MoS$_2$, except possibly for Mn. There was a complete absence of Fermi-level pinning, judging from the variation of E_F over a 1.5-eV range. An index of interface behavior $S'=1.28\pm0.22$ was determined from a plot of the Mo $3d_{5/2}$ and S $2p_{3/2}$ binding energies as a function of the Pauling electronegativity of the metal, which may represent a metal-semiconductor interface that operates close to the Schottky limit.[36]

This S' value was anomalously large for a covalent semiconductor when compared to other covalent semiconductors that exhibit strong Fermi-level pinning ($S'\lesssim0.3$). This hitherto unobserved behavior for a covalent semiconductor is attributed to the extreme unreactivity of the MoS$_2$(0001) surface that results from its hexagonal, two-dimensional layered structure. The S' value for MoS$_2$ was also compared with $\bar{S}$ ($=S'/A$)-versus-ϵ_∞^{-1} data for other semiconductors. The S' value for MoS$_2$ lays well above the theoretical limit of $S'=\epsilon_\infty^{-1}$, suggesting that, in agreement with Tersoff,[14] lack of Fermi-level pinning is due to poor interfacial bonding.

Various metals were also deposited on the MoS$_2$(0001) surface after it had been bombarded with 10-keV Ar$^+$ ions. Although high defect densities were produced ($\gtrsim4\times10^{14}$ cm^{-2}), little pinning of E_F was observed. There was, however, some evidence of chemical reaction as a result of the disruption of the inert MoS$_2$(0001) surface by ion bombardment.

Correlation of our results with present theories of Schottky-barrier formation confirms that chemistry at the metal-semiconductor interface is the crucial factor. However, in addition to thermodynamics, the orientation and structure of the surface (i.e., kinetics) must also be taken into account.

ACKNOWLEDGMENTS

This work was supported by the U.S. Air Force Space Division, Contract No. F04701-82-C-0083. The authors thank Dr. P. A. Bertrand for her assistance with the interpretation of the molecular-orbital theory, J. E. Childs for his help in operating the x-ray photoelectron spectrometer, Dr. H. K. A. Kan for helpful discussions related to the original concept for the experiments, and Dr. A. Taleb-Ibrahimi and Dr. J. F. McGilp for helpful comments. We are grateful to Dr. M. S. Leung and Dr. G. W. Stupian for helpful discussions on Schottky-barrier formation. We gratefully acknowledge Professor T. C. McGill for permission to reproduce a figure from Ref. 10 (our Fig. 1).

---

[1] W. Schottky, Naturwissenschaften **26**, 843 (1938).

[2] J. Bardeen, Phys. Rev. **71**, 717 (1947).

[3] P. W. Chye, I. Lindau, P. Pianetta, C. M. Garner, C. Y. Su, and W. E. Spicer, Phys. Rev. B **18**, 5545 (1978).

[4] P. Skeath, C. Y. Su, I. Hino, I. Lindau, and W. E. Spicer, Appl. Phys. Lett. **39**, 349 (1981).

[5] V. Heine, Phys. Rev. **138**, A1689 (1965).

[6] S. G. Louie, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. B **15**, 2154 (1977).

[7] J. Tersoff, Phys. Rev. Lett. **52**, 465 (1984).

[8] R. Ludeke, D. Straub, F. J. Himpsel, and G. Landgren, J. Vac. Sci. Technol. A **4**, 874 (1986).

[9] C. A. Mead, Solid-State Electron. **9**, 1023 (1966).

[10] S. Kurtin, T. C. McGill, and C. A. Mead, Phys. Rev. Lett. **22**, 1433 (1969).

[11] M. Schluter, Phys. Rev. B **17**, 5044 (1978).

[12] L. J. Brillson, Surf. Sci. Rep. **2**, 123 (1982).

[13] J. C. Phillips, J. Vac. Sci. Technol. **11**, 947 (1974).

[14] J. Tersoff, Phys. Rev. B **32**, 6968 (1985).

[15] *CRC Handbook of Chemistry and Physics,* 64th ed., edited by R. C. Weast (CRC Press, Boca Raton, FL, 1983), pp. E92–E95.

[16] A. L. Allred, J. Inorg. Nucl. Chem. **17**, 215 (1961).

[17] R. F. Frindt and A. D. Yoffe, Proc. R. Soc. (London), Ser. A **273**, 69 (1963).

[18] D. E. Haycock, D. S. Urch, and G. Wiech, J. Chem. Soc. Faraday Trans. 2 **75**, 1692 (1979).

[19] K. Suzuki, M. Soma, T. Onishi, and K. Tamaru, J. Electron Spectrosc. Relat. Phenom. **24**, 283 (1981).

[20] S. M. Davis and J. C. Carver, Appl. Surf. Sci. **20**, 193 (1984).

[21] I. T. McGovern, E. Dietz, H. H. Rotermund, A. M. Bradshaw, W. Braun, W. Radlik, and J. F. McGilp, Surf. Sci. **152/153**, 1203 (1985).

[22] *NBS Tables of Chemical Thermodynamic Properties,* edited by D. D. Wagman, W. H. Evans, V. A. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall, J. Phys. Chem. Ref. Data **11** (Suppl. 2) (AIP, New York, 1982).

[23] C. H. P. Lupis, *Chemical Thermodynamics of Materials* (North-Holland, New York, 1983), Appendix 3.

[24] J. H. Pugh and R. S. Williams, J. Mater. Res. **1**, 343 (1986).

[25] P. A. Bertrand, W. J. Kalinowski, L. E. Tribble, and L. U. Tolentino, Rev. Sci. Instrum. **54**, 387 (1983).

[26] C. S. Fadley, in *Electron Spectroscopy: Theory, Techniques, and Applications,* edited by C. R. Brundle and A. D. Baker (Academic, New York, 1978), pp. 72 and 73.

[27] See, for example, Y. Tanishiro, H. Kanamori, K. Takayanagi, K. Yagi, and G. Honjo, Surf. Sci. **111**, 395 (1981).

[28] J. R. Lince, D. J. Carré, and P. D. Fleischauer, Langmuir **2**, 805 (1986).

[29] R. T. Sanderson, *Inorganic Chemistry* (Reinhold, New York, 1967).

[30] A. L. Allred and E. G. Rochow, J. Inorg. Nucl. Chem. **5**, 264 (1958).

[31] *X-ray Photoelectron Spectroscopy,* edited by C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, and G. E. Muilenberg (Perkin-Elmer, Eden Prairie, MN, 1979), p. 104.

[32] L. J. Brillson, Phys. Rev. B **18**, 2431 (1978).

[33] G. J. Hughes, A. McKinley, R. H. Williams, and I. T. McGovern, J. Phys. C **15**, L159 (1982).

[34] W. Pong and D. Paudyal, Phys. Rev. B **23**, 3085 (1981).

[35] C. A. Mead and T. C. McGill, Phys. Lett. **58A**, 249 (1976).

[36] M. L. Cohen, J. Vac. Sci. Technol. **16**, 1135 (1979).

[37] A. M. Cowley and S. M. Sze, J. Appl. Phys. **36**, 3212 (1965).

[38] S. Kurtin and C. A. Mead, J. Phys. Chem. Solids **29**, 1865 (1968).

[39] J. M. Ziman, *Principles of the Theory of Solids,* 2nd ed. (Cambridge University Press, London, 1972), pp. 148 and 149.

[40] *Handbook of Optical Constants of Solids,* edited by E. D. Palik (Academic, Orlando, FL, 1985).

[41] J. R. Lince and P. D. Fleischauer, Proceedings of the 33rd National Symposium of the American Vacuum Society, Baltimore, Maryland, 1986 [J. Vac. Sci. Technol. (to be published).

[42] A. Zur, T. C. McGill, and D. L. Smith, Phys. Rev. B **28**, 2060 (1983).

[43] H. Dimigen, H. Hubsch, P. Willich, and K. Reichelt, Thin Solid Films **129**, 79 (1985).