

Photoemission study of Cr on *a*-Si:H

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We report a synchrotron-radiation photoemission study of Cr evaporated on rf-sputtered *a*-Si:H at room temperature. The evolution of the interface qualitatively follows that on *c*-Si, despite differences in the valence-band emission. The interface begins with an inactive layer ($\leq 1 \text{ \AA}$) of Cr, followed by an intermixed Cr/*a*-Si:H layer ($\leq 12 \text{ \AA}$). With further Cr deposition, bulklike Cr metal begins to develop on top of these. Some features exhibited by the Cr/*a*-Si:H interface are specific to *a*-Si:H surfaces. For instance, Cr adatoms are found around the dangling-bond neighborhood at coverages below 1 \AA , avoiding Si-H bonds. The oxygen residue is responsible for the presence of a 6-eV peak in the valence band as well as a chemical shift in the Si $2p$ core levels. However, it is the intermixed Cr/*a*-Si species occurring above 2 \AA of Cr deposition that provoke the presence of the structures, even though at low coverages, the oxygen residue does not show any effect on the surface-electronic structure of the *a*-Si:H film. At high coverage, a slight trace of silicon atoms is still detectable.

INTRODUCTION

Detailed photoemission studies of the electronic structure of the Cr/*c*-Si interface have been reported by a number of groups.¹⁻³ The consensus picture for the evolution of the interface is an initial inert Cr layer, followed by an intermixed layer and, ultimately, the development of bulk Cr metal, with increasing coverage. The inert threshold coverage has been shown to be essential to the formation of the following intermixed layer. The latter has exhibited silicidelike valence bands. The eutectic temperature for a CrSi₂ phase is about 450 °C. The intermixed layer has shown a great degree of instability when exposed to oxygen.^{3,4}

As far as we know, the Cr/*a*-Si:H interface has yet to be explored. In what follows, we report photoemission measurements using synchrotron radiation to study the room-temperature interface formation of Cr evaporated on *a*-Si:H. The purpose of the current study is twofold: one is to serve as a complement of the study of the crystalline interface and the other is a comparison with our previous Au/*a*-Si:H study⁵ in order to understand better metal/*a*-Si:H interfaces. It is well known that the properties of *a*-Si:H films are process determined.⁶ Some unique features can be found, such as surface enrichment of hydrogen diffused from the bulk⁷ and instability of the free surface.⁸ Therefore, we do not expect the Cr/*a*-Si:H interface to behave exactly as its crystalline counterpart. Nevertheless, in the following, close comparisons with the Cr/*c*-Si and with the Au/*a*-Si:H interfaces will be made.

EXPERIMENT

The experiment was performed at the Synchrotron Radiation Center, University of Wisconsin. Monochromatized radiation was incident from a Seya/ERG (extended-range grasshopper monochromator) beam

line,⁹ scannable from 5 to over 1000 eV. The details of the experiment, including sample preparation and data acquisition, can be found elsewhere.⁵ In short, a $2.2\text{-}\mu\text{m}$ *a*-Si:H film made in a rf plasma chamber and sputtered clean in the data-acquisition chamber was mounted as the substrate for a series of Cr depositions under a pressure of 8.5×10^{-11} Torr. The pressure never exceeded 3.5×10^{-10} Torr in obtaining a thick film. Measurements were always made below 5×10^{-11} Torr. Thicknesses reported are those of an equivalent uniform homogeneous layer of Cr and are integrated thicknesses for successive evaporations. Photoelectron energy distribution curves (EDC's) were analyzed with a double-pass cylindrical mirror analyzer. The integrated intensity of the O 1s line of the oxygen residue on the *a*-Si:H substrate before Cr evaporation was $\sim 3\text{--}4\%$ of that of the Si $2p$ line.

RESULTS AND DISCUSSION

We present some representative EDC's in Figs. 1-4. The changes of the valence-band EDC's with Cr deposition are shown in Figs. 1 and 2, with photon energies of 21 and 55 eV, respectively. From the figures, it is clear that the 21-eV photon energy scan emphasizes the Cr $3d$ states, as well as the lower part of the Si valence band. However, at coverages below 6 \AA , features more than 6 eV below the Fermi level, E_F , are severely distorted by the secondary electron emission as well as by the contribution from argon atoms. The argon peak, at about 9 eV below E_F , is a residue of the sample preparation. Spectra taken at $h\nu=55$ eV manifest clearly the emission from the lower part of the valence band.

Core-level spectra are shown in Figs. 3 and 4. The former, taken at a photon energy of 110 eV, are to monitor the emission from the Cr $3p$ states, while the latter, taken at $h\nu=160$ eV, are for the Si $2p$ states. The photon energies were selected to enhance surface sensitivity, with an escape depth on the order of 5 \AA . The combined reso-

lution of the monochromator and the energy analyzer is about 330 meV for $h\nu=160$ eV and 210 meV for $h\nu=110$ eV. All spectra are normalized to the photon flux and further scaled in the figure in accordance with the same magnitude. Initial-state energies are referred to E_F .

LOW COVERAGE ($\leq 2 \text{ \AA}$)

As shown in Fig. 2, a "clean" a -Si:H spectrum has features at about 3 and 6.5 eV, which are associated with the emission from Si $3p$ states and bonding states of Si $3p$ -H $1s$, respectively.⁵ Figure 3 shows that the energy

of the substrate Si $2p_{3/2}$ line at the highest intensity is 99.6 ± 0.1 eV. Because of possible effects from oxygen, we review previous work on the effects of oxygen in a -Si:H films. Kärcher and Ley¹⁰ reported that the oxygen-induced spectral contributions appeared at 6.7 and 8.0 eV in oxygen-doped a -Si:H. Yang *et al.*¹¹ reported that for an a -SiO_x:H film, the O $2p$ character was at 7 eV. The absence of these features in Fig. 1 explicitly indicates that residual oxygen does not significantly influence the electronic states of the a -Si:H substrate. Note that the cross section of the Si-O bond at $h\nu=21$ eV has been claimed to be at least 15 times higher than that of Si-Si or Si-H bonds.¹⁰ Bulk sensitive scans at $h\nu=110$ eV (not shown) show no states due to chemical shifts either.

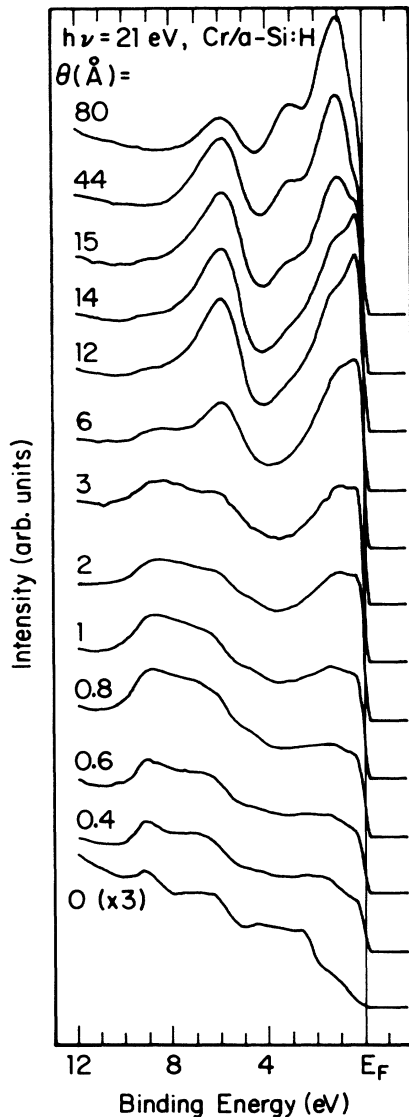


FIG. 1. Valence-band spectra taken at $h\nu=21$ eV. The number in the high-binding-energy end gives the Cr thickness in angstroms. All spectra are normalized to photon flux and then adjusted to the maximum magnitude at 80 Å. Note that the Cr $3d$ -derived states already dominate the vicinity of the Fermi level on the EDC's at the onset of the deposition. The Fermi level appears at 0.2 Å.

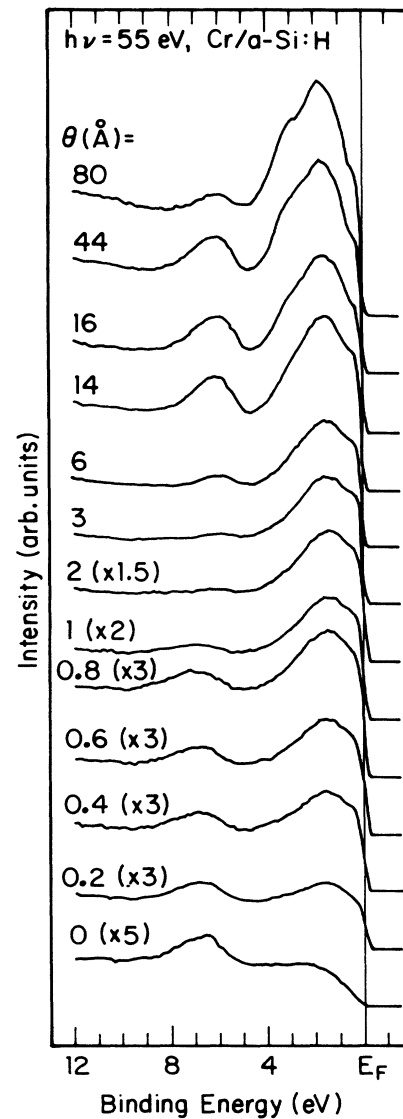


FIG. 2. Valence-band spectra taken at $h\nu=55$ eV to enhance the contribution in the lower part of the valence band at low coverage. Normalization scheme is the same as in Fig. 1. The bonding states due to Si $3p$ and H $1s$ orbitals are visible at coverages below 1 Å.

Upon Cr deposition, it is evident from Figs. 1 and 2 that the emission from the Cr 3*d* orbitals promptly dominates the vicinity of the Fermi-level region. More significantly, a Fermi level appears at the lowest coverage, 0.2 Å. As the Cr coverage increases, two peaks, initially located at 1.5 and 0.5 eV at the lowest coverage, move progressively toward E_F and are finally stable at 1.05 and 0.38 eV, respectively, above 2 Å. In the same coverage (from 0.2 to 2 Å), Figs. 3 and 4 show that the energies of the Cr 3*p* and Si 2*p* core levels remain unchanged. The binding energy of the Cr 3*p* line is 42.0 eV. There is less than 0.1 eV variation of the Si 2*p* lines with coverage, and that is mostly due to the intensity modulation of the Si 2*p* states in SiH_{*x*} (0 ≤ *x* ≤ 3) complexes. As a consequence, we do not regard the variation as due to band bending, in line with the valence-band results.

The Cr 3*d*–Si 3*p* bonding and nonbonding structures with different silicide stoichiometries in the Cr/*c*-Si system have been studied theoretically² and experimentally.^{2,3} Density-of-states calculations² infer that the bonding state in a Si-rich silicide has a higher binding energy than in a Cr-rich silicide. Experimental study of a definite silicide like CrSi₂ using photoemission reveals the binding energies of the bonding and nonbonding states to be 2.2 and 0.2 eV, respectively.³ Different values have also been given, 1.7 and 0.3 eV, respectively.² Wetzel *et al.* further showed the bonding and nonbonding states for CrSi were 1.6 and 0.2 eV, respectively.³ For a photoemission study of a Cr/*c*-Si interface formed by evaporation at room temperature, the binding energy of the bonding state shifted progressively toward the Fermi level with increasing coverage. The negative shift appeared

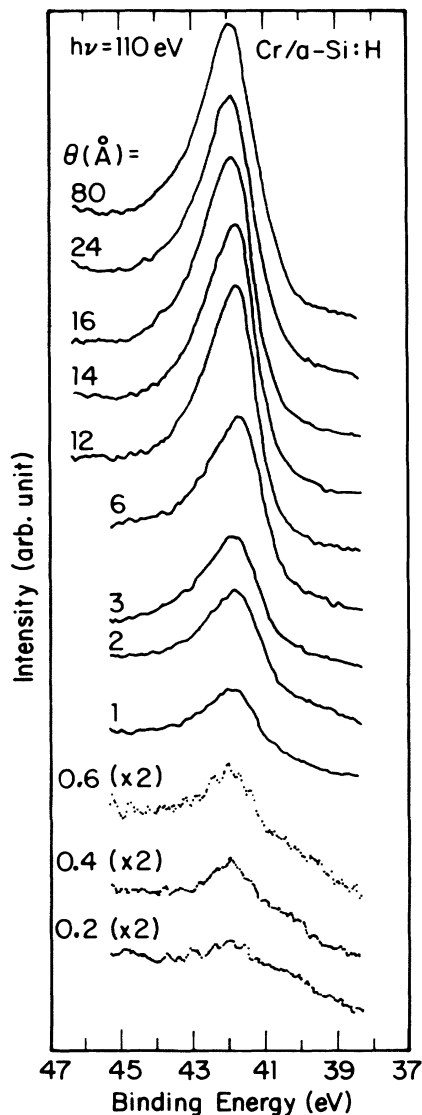


FIG. 3. Surface-sensitive core-level EDC's taken at $h\nu = 110$ eV to monitor the emission from the Cr 3*p* line.

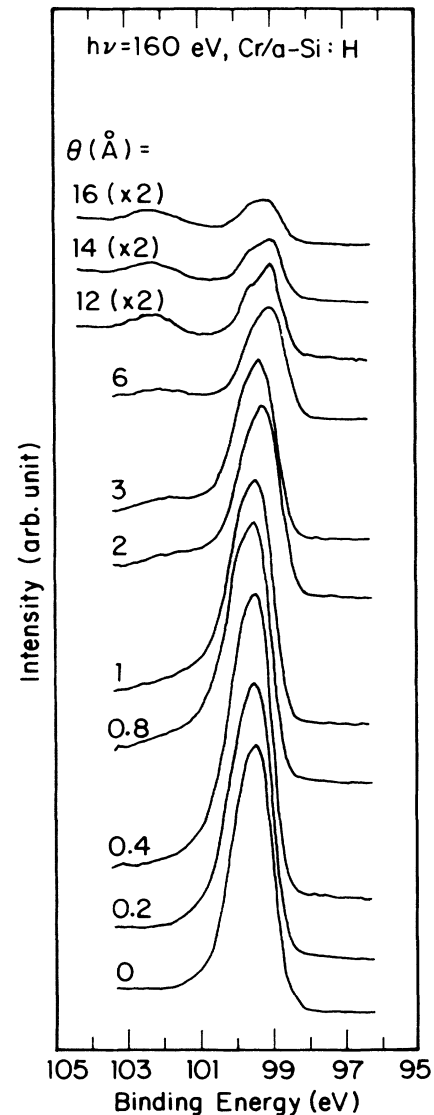


FIG. 4. Surface-sensitive core-level EDC's taken at $h\nu = 160$ eV to monitor the emission from the Si 2*p* states.

only in a reacted Ci-Si region whose thickness was given as 10–15 monolayers (ML) by Franciosi *et al.*² and as 25 ML by Wetzel *et al.*³

Our room-temperature Cr/*a*-Si:H system shows a similar shift of states at 2 eV below E_F with increasing coverage (Fig. 1). We do not, however, regard it as an indication of change in stoichiometry or the existence of a bonding state. Rather, we interpret it as a signature of increasing *d* orbital overlap. Concurrent with stoichiometry changes in the valence band, Si, as well as Cr, core levels should exhibit shifts, usually to lower binding energy.^{2,3} As seen in Figs. 3 and 4, the Si 2*p* and Cr 3*p* lines have no such shifts upon bonding changes, due neither to chemical reactions nor to an adjustment of the band edge. This leads us to believe that the shift of the valence states within 2 eV comes from increasing *d*-orbital overlap¹² instead of stoichiometry changes along the surface normal. The line shape in Fig. 2 further supports our interpretation. For a Si-rich silicide, an EDC taken at a photon energy of 50 eV shows that the intensity of the nonbonding state is higher than that of the bonding state.¹³ In Fig. 2, no such feature appears (our data at $h\nu=50$ eV exhibit the same shape as in Fig. 2).

In addition to the development of the Cr 3*d* states, the emission from the Si-H states near 6.5 eV is still seen unambiguously (Fig. 2). Its persistence needs further comment. As one can see, the 6.5-eV emission from the substrate is at a photon energy where the cross section of the *d* orbitals is predominant. One might argue that the Cr 3*d* and Si-H bonding orbitals appear in different regions in the valence band, reducing the probability of their interfering destructively with each other. However, as shown in Fig. 2, the scaling factor for the spectra is reduced at low coverage (spectra were normalized with respect to 80-Å thickness). The 6.5-eV Si-H bonding state, even so, can be recognized easily without tuning the photon energy to depress the *d*-orbital emission, as in the case of Au or Ag deposits.⁵ Thus, the survival of the Si-H states at a photon energy with high *d*-orbital cross section suggests that the sites of the Cr atoms must be those with no Si-H complex in the neighborhood. In other words, they gather around the sites where dangling bonds are dominant. This also suggests that Cr adatoms do not have a long-range effect on the electronic states of the *a*-Si:H surfaces. The implication is even clearer as we increase coverage. The intensity of the Cr 3*d* states increases with increasing coverage. The intensity of the 6.5-eV peak, however, does not attenuate in proportion. Note that the 6.5-eV peak is seen only at a coverage less than 1 Å, which has a low average metal density on the surface.

The less hybridized Cr 2*d*-Si 3*p* feature in the low-coverage region in the Cr/*a*-Si:H system can be explained by the great difference in the density of dangling bonds of the *c*-Si and *a*-Si:H surfaces. Considering the Cr adatoms gathered only in the dangling-bond neighborhoods at this low coverage, we obtain a higher *local* density of Cr adatoms in an *a*-Si:H surface than in a crystalline surface. In other words, those bonding sites are in a region of Cr enrichment, thereby giving the bonding state a lower binding energy.

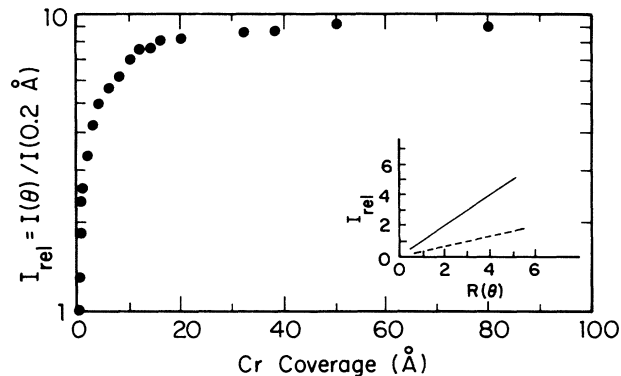


FIG. 5. Integrated intensity of the Cr 3*p* state normalized to the value at 80 Å as a function of coverage Θ . Inset shows the reduced intensity, $I_{rel} = I(\Theta) / I(0.2 \text{ \AA})$, vs reduced coverage, $R(\Theta) = \Theta / 0.2 \text{ \AA}$, at low exposures. The solid line indicates nonintermixed, homogeneous growth on a smooth surface.

Clustering and yet intermixing of Cr adatoms is conceivable in Fig. 5 as well, where the integrated Cr 3*p* intensity scaled to the intensity at 0.2 Å is shown. The inset emphasizes the reduced intensity, $I_{rel} = I(\Theta) / I(0.2 \text{ \AA})$, versus reduced coverage, $R(\Theta) = \Theta / 0.2 \text{ \AA}$, at low exposures, with the solid line indicating nonintermixed, homogeneous growth on a smooth surface. It is evident from the figure that at low coverages, the Cr 3*p* intensity (dashed line) does not rise proportionally with coverage. The deviation can be understood as follows. In a submonolayer region, the intensity of an overlayer increases linearly with coverage, thereby giving a slope of unity in \AA^{-1} for the solid line in the inset of Fig. 5. However, if the overlayer is thick enough to form clusters, then the escape-depth effect needs to be considered. As a result, the slope of the solid line would be 0.28 \AA^{-1} if the geometric factor is included. This value is consistent with the slope of the actual data (dashed) 0.27 \AA^{-1} . Therefore, the impinging Cr atoms are clustered on the surface at coverage below 1 Å.

In conclusion, as illustrated by the valence-band as well as core-level spectra, at low coverage, Cr adatoms gather in the neighborhoods of dangling bonds, thereby giving a local Cr-rich environment. Strong bonding between the overlayer and the substrate does not occur. Further, the clusters are metallic.

INTERMEDIATE ($\leq 12 \text{ \AA}$) AND HIGH COVERAGES ($\geq 12 \text{ \AA}$)

At coverage above 2 Å, the Cr 3*d* states continue to give rise to strong transitions at 0.38 and 1.05 eV, as seen in Figs. 1 and 2. The 6.5-eV Si-H bonding state disappears in the valence band. In Fig. 2 ($h\nu=55$ eV), the line shape and positions of the Cr 3*d* band are essentially the same. Only the intensity increases with increasing coverage. Figure 1 ($h\nu=21$ eV), however, shows different behavior of the occupied *d* band. The main features are (1) the bandwidth gradually broadens from 3.8 eV at 3 Å to

4.35 eV at 12 Å and stays constant thereafter; (2) the bonding and nonbonding states exhibit intensity modulations; and (3) a peak at 3.07 eV starts to develop at 12 Å. In addition, both Figs. 1 and 2 show that a peak centered at 6 eV appears in the spectra.

As to core levels, Figs. 3 and 4 show displacements of both the Si 2*p* and Cr 3*p* lines. Referring to the bulk position of the Cr 3*p* line at the highest coverage (42.0 eV), we can see that it gradually shifts to lower binding energies at coverages above 2 Å, but moves back to the bulk energy above 12 Å. It is at 42.0 eV above 16 Å with no further change in position. The Si 2*p* line, referred to the line position at the highest intensity at the zero coverage (99.6 eV), shifts to lower binding energy above 2 Å, but stays fixed at 99.0 eV afterwards. As indicated in Refs. 2 and 3, a shift to lower binding energy of the substrate Si 2*p* states normally occurs in an intermixed or silicide-like interface. Therefore, an intermixed or silicide-like Cr/*a*-Si:H layer may be present above 2 Å. Later, we will show other behavior that differentiates these.

Although the width of the Cr 3*d* states increases, it is still less than that of the calculated one-particle density of states.² A number of studies have shown that Coulomb correlation is important for the Cr 3*d* states, in Cr silicides as well as in crystalline Cr.^{15,16} Considering correlation effects in the calculation allows the bonding and nonbonding peaks to move toward E_F , and reduces the intensity of the bonding structure dramatically. A similar correlation effect is expected for the Cr/*a*-Si:H interface.

To better illustrate the valence-band feature (2), we show the peak-height intensities of the nonbonding (0.38 eV) and bonding (1.05 eV) states in Fig. 6. Points in Fig. 6 were normalized to the value at 0.4 Å. Note that the bonding state is involved to a lesser extent than the case of *c*-Si. As shown in Fig. 6, the intensity of the bonding state increases linearly at low coverage and becomes nearly constant at high coverage. The intensity of the nonbonding state, on the other hand, evolves differently. It rises to a maximum at 12 Å and drops to saturation afterwards. The intensity evolution of the nonbonding

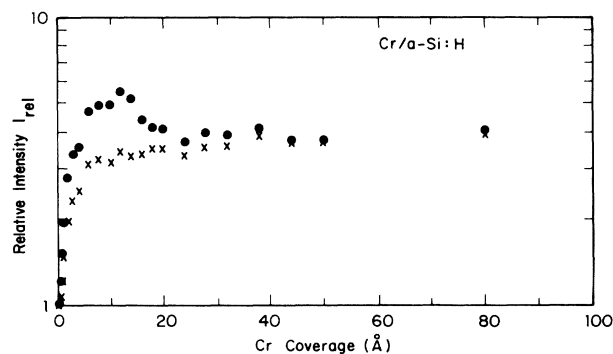


FIG. 6. Intensity evolutions of the 0.38 eV (●) and 1.05 eV (×) peaks in the valence band. Data are taken from Fig. 1 (see text). Note that a maximum intensity occurs at 12 Å for the 0.38-eV peak.

state is quite different from the case of *c*-Si. In the Cr/*c*-Si interface, the intensity of the bonding state at $h\nu=21$ eV is always higher than that of the nonbonding state, and no turnover in intensity of the nonbonding state such as that in Fig. 6 has been reported.² Even though the bonding-state emission is weaker in a definite silicide like CrSi₂, its binding energy is located 0.5 eV higher than in the Cr/*c*-Si interface formed at room temperature. Therefore, based on the behavior of the valence band, we find that the criteria for silicide formation set by the Cr/*c*-Si interface are hardly applicable to the Cr/*a*-Si:H interface. Nevertheless, the interface is an intermixed one but to a lesser degree, a statement reinforced by core-level behavior. In addition, if a Cr 3*d*-Si 3*p* bonding state were formed, then the hybrid would have a higher binding energy than either of the states.¹⁵ As shown in Fig. 1, the supposed bonding state is located at 1.05 eV, starting from 2 Å until bulk Cr forms. As discussed below, we attribute the 6-eV structure to oxygen.

Switendick¹⁷ has made a density-of-states calculation for a hexagonal CrH. It showed that excess electrons from hydrogen would be added to a system, moving the Fermi level upward and subsequently lower the density of states at E_F . Moreover, a hydrogen-induced feature would occur 6–7 eV below the Fermi level. In our system, a CrH compound is possibly formed. Although a new feature at about 6 eV appears, the behavior at E_F does not match the calculated prediction, so we cannot confirm that a hexagonal CrH phase is formed in the Cr/*a*-Si:H interface.

In Fig. 4, at 2-Å thickness, a weak hump appears on the high-binding-energy side of the substrate Si 2*p* line, 2.7 eV higher. The chemical shift becomes even larger with increasing coverage. However, the separation, due partially to a shift of the hump itself to higher binding energy and partially to the displacement of the substrate Si 2*p* line to lower binding energy, becomes constant at 3.2 eV above 12 Å. The intensity of the chemically shifted peak increases with increasing coverage until the development of bulk Cr. Along with the presence of the chemically shifted peak in the neighborhood of the Si 2*p* core levels, valence-band emission (Figs. 1 and 2) shows a 4-eV-wide feature centered at about 6 eV below E_F . Its intensity evolved similarly to the chemically shifted Si 2*p* peak, increasing with increasing coverage, suggesting that it might be caused by Cr itself or by the Cr/Si interface.

The presence of the chemically shifted Si 2*p* structure is somewhat surprising. According to the magnitude of the shift, it is possibly an oxide-driven feature. However, as shown in the valence-band as well as core-level spectra, no oxygen effects appear at low coverages. Furthermore, the energy positions induced by the oxygen do not correspond to those found in the study of the oxidation of Cr (Ref. 18) and *c*-Si (Ref. 19) and Cr/*c*-Si,²⁰ or *a*-SiO_x:H.¹¹ Nevertheless, other evidence (see below) suggests that it really is oxygen induced. Excluding the Cr evaporator as its origin (pressure always below 8.5×10^{-11} Torr), we speculate that the oxygen residual was incorporated during *a*-Si sample preparation in the rf sputtering chamber. In an abrasion study, Ballataud *et al.*²¹ have illustrated

that a hydrogenated silicon sample made by rf sputtering shows traces of oxygen after 500 Å of the film has been milled away by argon bombardment. Moreover, they found that the oxygen does not induce any chemical or substrate shift of the Si 2*p* core levels. Similar features are also observed empirically in our study. We measured intermittently the emission from the oxygen *K* edge and found a proportional increase in intensity with increasing chemical-shift intensity. This gives further evidence that the chemically shifted peak is due to Si atoms reacting with oxygen which are from the substrate itself.

Franciosi *et al.*⁴ have illustrated that the oxidation rate increases in the Cr/*c*-Si interface after a critical Cr thickness. Wetzel *et al.*³ have further found that oxygen uptake for a Cr/*c*-Si interface formed at 300 K is at least tenfold greater than for stoichiometric silicides. The intermixed Cr/Si layer has been claimed responsible for the increased oxidation.^{3,4} In the Cr/*a*-Si:H system, we obtain an unreacted thickness at 1 Å of deposition. Above that, the interface has become an intermixed one. Therefore, referring to the Cr/*c*-Si study, we suggest that the residual oxygen undergoes a reaction provoked by the intermixed Cr/*a*-Si:H interface to form amorphous-silicon oxide, *a*-SiO_{*x*}, where *x* is less than 1.²² The more the intermixed product, the higher the emission of the oxidized state.

A 6-eV peak has also appeared on Cr metal itself²³ and CrSi₂.² However, its origin has been controversial. For CrSi₂, Weaver *et al.*² have attributed it to a Si *p* state. For Cr metal, some groups²³ have discussed it as a valence-band satellite, while another²⁴ has proven that it is due to oxygen 2*p* states. The explanation is hindered by the fact that the 6-eV peak in Cr metal shows resonant behavior near the photon energy of the 3*p*-3*d* threshold transition energy and a correlation effect takes place in the *d* band. However, as indicated in the work of Raaen and Murgai,²⁴ the 6-eV peak is absent in a polycrystalline Cr film. With the clean surface exposed to oxygen, the 6-eV peak starts to appear. They have further shown that the oxidized surface resonates when the photon energy sweeps through the Cr 3*p*-3*d* transition, identical to other reports.²³ We have observed a similar resonantlike enhancement of the 6-eV peak at low (6 Å) and high (120 Å) Cr coverages. Therefore, with the heritage of the residual oxygen in our system and with assistance of the study in Ref. 24, we can assign the 6-eV peak to an oxygen-induced structure. Further, carefully examining the evolution of the valence band, we find the presence of the 6-eV peak does not inhibit the emission of the Cr 3*d* states. In other words, the oxygen does not bond strongly with the Cr overlayer to give rise to Cr₂O₃. Otherwise, the emission near the Fermi level would attenuate drastically.¹⁸

In summary, the 6-eV peak in the valence band and the chemical shift of the Si 2*p* line are believed to be due to oxygen. The 6-eV peak also appears in the Sm/*a*-Si:H interface after a certain thickness.²⁵

The intermixing effect exhibited in the Cr/*a*-Si:H system is certainly not found in our study of the Au/*a*-Si:H system.⁵ In the latter, the interface also became intermixed above 2 Å of Au deposition. However, no

oxygen-induced features like the 6-eV peak in the valence band or the chemically shifted peak in the core-level spectra appeared in that study. This clearly indicates that the intermixed Cr/Si species are less stable.

After the intermixed overlayer, bulk Cr starts to develop after 12 Å of Cr deposition. The evidence is as follows: (1) the intensity of the nonbonding state begins to fall from a maximum at 12 Å; (2) a feature at 3.07 eV in the valence band starts to develop at 12 Å; (3) the bandwidth of the Cr 3*d* states does not increase above 12 Å; and (4) the intensity of the Cr 3*p* state stays nearly constant above 12 Å (Fig. 5). Despite the development of bulk Cr, silicon atoms can still be detected. At 80 Å of Cr coverage, there are slight traces of silicon atoms. Silicon at this coverage can be thought of as atoms that diffuse through the interface. Interface-controlled diffusion occurs in the case of *c*-Si as well.³

CONCLUSION

We have studied a Cr/*a*-Si:H interface formed at 300 K using valence-band as well as core-level spectroscopy. At coverages below 1 Å, the interface is inert. But the surface has become metallic at as little as 0.2-Å effective thickness. Moreover, Cr adatoms cluster in the vicinity of the Si that is not bonded with hydrogen. Above 2 Å, the Cr overlayer begins to intermix with the *a*-Si:H substrate, but to a lesser degree than the crystalline counterpart. No definite silicides can be identified in this region. This statement is reinforced by the study of Nava, Tien, and Tu,²⁶ who showed that the CrSi₂ film is a semiconductor. Because of the inevitable incorporation of oxygen in the *a*-Si:H substrate in the hydrogen plasma, the intermixed Cr/Si layer serves as a catalyst to increase the rate of the interaction between the residual oxygen and elemental silicon. The residual oxygen initially does not have a chemical effect on the substrate. The thickness of the intermixed layer is about 12 Å. Above that, a bulk-like Cr feature develops. A slight trace of silicon atoms is still found at a thickness of 80 Å.

It is noteworthy that because of the intrinsic properties of the *a*-Si:H sample, such as an aging effect⁸ and the phenomenon of H atoms diffusing from the bulk,⁷ we found the intensities of the 6-eV peak and the chemically shifted Si 2*p* line increased overnight at a fixed Cr thickness.²⁷ Changes overnight occurred to the Au/*a*-Si:H system as well, which shows quantitative differences of the interface built by processes of one or several accumulated depositions to a given thickness. To obtain the same line shapes in the valence-band or the core-level spectra from these two processes requires less thickness for the single-deposition mode than for the accumulated-deposition mode.²⁷ Another similarity of Au and Cr deposits lies in the way adatoms distribute on the surface. They are likely to be dispersed on the *a*-Si:H surface around the neighborhood where dangling bonds dominate, avoiding the Si-H bonding complexes. In other words, in the area where Si-H dominates, no sites are available for adatoms to bond. However, surface roughness²⁸ increases the densities of valleys, steps, kinks, or microvoids. Those are the regions that are likely to attract diffused adatoms.

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- ¹A. Franciosi, D. J. Peterman, and J. H. Weaver, *J. Vac. Sci. Technol.* **19**, 657 (1981).
- ²A. Franciosi, D. J. Peterman, J. H. Weaver, and V. L. Moruzzi, *Phys. Rev. B* **25**, 4981 (1982); A. Franciosi, J. H. Weaver, D. G. O'Neill, F. A. Schmidt, O. Bisi, and C. Calandra, *ibid.* **28**, 7000 (1983); J. H. Weaver, A. Franciosi, and V. L. Moruzzi, *ibid.* **29**, 3293 (1984).
- ³P. Wetzel, C. Pirri, J. C. Peruchetti, D. Bolmont, and G. Gewinner, *J. Vac. Sci. Technol. A* **5**, 3359 (1987).
- ⁴A. Franciosi, S. Chang, P. Phillip, C. Caprile, and J. Joyce, *J. Vac. Sci. Technol. A* **3**, 933 (1985).
- ⁵T.-W. Pi, A.-B. Yang, C. G. Olson, and D. W. Lynch, preceding paper, *Phys. Rev. B* **42**, XXX (1990).
- ⁶J. Stuke, *Ann. Rev. Mater. Sci.* **15**, 79 (1985) and references therein; K. Tanaka and A. Matsuda, *Mater. Sci. Rep.* **2**, 139 (1987).
- ⁷M. Láznicka, *Surf. Sci.* **87**, L269 (1979).
- ⁸H. Oheda, *Phys. Rev. B* **39**, 10 179 (1989).
- ⁹C. G. Olson, *Nucl. Instrum. Methods, Phys. Res. Sect. A* **266**, 205 (1988).
- ¹⁰R. Kärcher and L. Ley, *Solid State Commun.* **43**, 415 (1982).
- ¹¹L. Yang, B. Abeles, W. Eberhardt, and H. Stasiewski, *Phys. Rev. B* **35**, 9395 (1987).
- ¹²S.-T. Lee, G. Apai, M. G. Mason, R. Benbow, and Z. Hurych, *Phys. Rev. B* **23**, 505 (1981); G. K. Wertheim, S. B. DiCenzo, and S. E. Youngquist, *Phys. Rev. Lett.* **51**, 2310 (1983); H. Roulet, J.-M. Mariot, G. Dufour, and C. F. Hague, *J. Phys. F* **10**, 1025 (1980); M. G. Mason, *Phys. Rev. B* **27**, 748 (1983).
- ¹³A. Franciosi and J. H. Weaver, *Physica B&C (Amsterdam)* **117-118B**, 846 (1983).
- ¹⁴C. Calandra and O. Bisi, *Phys. Rev. B* **31**, 8288 (1985); C. Calandra, O. Bisi, U. Del Pennino, S. Valeri, and Y. Xi, *Surf. Sci.* **168**, 164 (1986).
- ¹⁵S. Valeri, L. Grandi, and C. Calandra, *J. Electron Spectrosc. Relat. Phenom.* **43**, 121 (1987).
- ¹⁶C. D. Gelatt, Jr., A. R. Williams, and V. L. Moruzzi, *Phys. Rev. B* **27**, 2005 (1983).
- ¹⁷A. C. Switendick, in *The Hydrogen in Metal I*, Vol. 28 of *Topics in Applied Physics*, edited by G. Alefeld and J. Volkl (Springer-Verlag, New York, 1979).
- ¹⁸G. Gewinner, J. C. Peruchetti, A. Jaegle, and A. Kalt, *Surf. Sci.* **78**, 439 (1978); **122**, 383 (1982).
- ¹⁹G. Hollinger and F. J. Himpsel, *J. Vac. Sci. Technol. A* **1**, 640 (1983).
- ²⁰P. Wetzel, C. Pirri, J. C. Peruchetti, D. Bolmont, and G. Gewinner, *Surf. Sci.* **178**, 27 (1986).
- ²¹D. Ballataud, G. Moulin, and M. Aucouturier, *Surf. Sci.* **178**, 70 (1986).
- ²²J. Finster, O. Schulze, and A. Meisel, *Surf. Sci.* **162**, 671 (1985).
- ²³J. Barth, F. Gerken, K. L. I. Kobayashi, J. H. Weaver, and B. Sonntag, *J. Phys. C* **13**, 1369 (1980); D. Chandris, J. Lecante, and Y. Petroff, *Phys. Rev. B* **27**, 2630 (1983); H. Sugawara, K. Naito, T. Miya, A. Kakizaki, I. Nagakura, and T. Ishii, *J. Phys. Soc. Jpn.* **53**, 279 (1984).
- ²⁴S. Raaen and V. Murgai, *Phys. Rev. B* **36**, 887 (1987).
- ²⁵A.-B. Yang, T.-W. Pi, C. G. Olson, and D. W. Lynch, unpublished.
- ²⁶F. Nava, T. Tien, and K. N. Tu, *J. Appl. Phys.* **57**, 2018 (1985).
- ²⁷T.-W. Pi, C. G. Olson, and D. W. Lynch, unpublished.
- ²⁸R. Wiesendanger, L. Rosenthaler, H. R. Hidber, H.-J. Güntherodt, A. W. McKinnon, and W. E. Spear, *J. Appl. Phys.* **63**, 4515 (1988).