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Interface catalytic effect: Cr at the Si(111)-Au interface

A. Franciosi and J. H. Weaver
*Department of Chemical Engineering and Materials Science, University of Minnesota,
Minneapolis, Minnesota 55455*

D. G. O'Neill
*Synchrotron Radiation Center, University of Wisconsin—Madison,
Stoughton, Wisconsin 53589*

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Synchrotron radiation photoemission studies of the effect of Cr interlayers on Si(111)-Au interface reaction show that Cr concentrations below 1×10^{15} atoms/cm^2 retard Si-Au intermixing, concentrations between 1 and 7.5×10^{15} atoms/cm^2 promote Si-Au intermixing, and concentrations in excess of 8×10^{15} atoms/cm^2 sharply reduce intermixing. These variations are shown to depend on the three formation stages of the Si-Cr junction. Cr itself is shown only to be indirectly involved in the Si-Au reaction and Si is to be the only moving species.

The driving forces responsible for atomic interdiffusion at Si-metal interfaces have been the subject of intense discussion.[1-6] To understand this atomic interdiffusion, we must identify the parameters that control interdiffusion kinetics and the junction profile, and we must determine the relationships that exist between these parameters and the chemical activity of the species involved in the interface formation process.[7-9]

In order to better understand interdiffusion, we performed an investigation of the effect of Cr interlayers on the atomic interdiffusion of Si and Au at the Si(111)-(2×1)-Au interface, with special emphasis on the chemical aspects of interdiffusion.

In this paper, we show that for Cr coverages from 2 to 9 Å the interlayer *promotes* the Si-Au intermixing, while the interdiffusion is *reduced* for Cr coverages above 9 Å (10 monolayers) or for coverages less than one monolayer. This strikingly nonmonotonic behavior rules out simple "diffusion barrier" effects and is related, instead, to the three stages of Si-Cr reaction. Each stage corresponds to a different morphology or microscopic arrangement of the Si atoms at the surface and, hence, a different energy content of the Si-Si bonds.

Our results show that the interlayer Cr atoms do not appear directly involved int the Si-Au reaction. Instead, since the Cr interlayer affects the formation of the Si-Au junction and its concentration modulates the Si-Au reaction, it seems natural to define the role of the Cr atoms as that of an "interface catalyst" for the Si-Au reaction.

The Si-Cr-Au system was chosen because the Si-Cr and the Si-Au interfaces are well characterized[10-13] and neither gives rise to island formation at room temperature. The relative surface concentration of the different species and the evolution of the chemical bonding was followed systematically through synchrotron photoemission from valence and core electronic states, both as a function of Au coverage and Cr interlayer thickness. The experiments were performed at the University of Wisconsin Synchrotron Radiation Center with a "Grasshopper" grazing-incidence monochromator for $40 \leq h\nu \leq 140$ eV. The photoelectrons were analyzed by a double-pass cylindrical mirror energy analyzer, and the overall resolution (monochromator + analyzer) was 0.3–0.5 eV. Cr and Au were evaporated *in situ* from W coils onto cleaved *n*-type Si crystals (P-doped, 10^{15} cm^{-3}) and the overlayer thickness was measured by a quartz-crystal monitor ($\theta_{\text{Cr}} = 1$ Å $= 1.1$ monolayers; $\theta_{\text{Au}} = 1$ Å $= 0.8$ monolayers; 1 monolayer $= 7.6\times10^{14}$ atoms/cm^2). Cr depositions of 0.5–15 Å were made immediately before a series of Au depositions (maximum Au coverage of 50–70 Å for each Cr interlayer thickness). All experiments were performed at pressures of 5×10^{-11} Torr ($\leq 6\times10^{-10}$ Torr during evaporation) and at room temperature.

In Fig. 1 we show representative photoelectron energy distribution curves (EDC's) for the valence band of the Si-Cr-Au interface at a fixed Au coverage of 20 Å as a function of Cr interlayer thickness.[14] The topmost spectrum corresponds to Si(111)-Au without Cr, and the bottom-most shows the valence bands for a 20-Å Au film on an inert substrate.[15] The differences between these two, which reveal the formation of the Si-Au interface, have been explained as modifications of Au 5*d*-derived density of states features caused by Si atoms in the Au matrix, mainly through the change of the *d*-*d* overlap.[12,14,16,17] Taking such differences[17] as a fingerprint of Si-Au reaction, the systematics in Fig. 1 show that a Si-Au reaction can occur in the presence of a Cr interlayer, but that the intermixing is sharply reduced when the interlayer thickness increases above 9 Å.

The presence of Si atoms in the Au matrix is clearly indicated by the topmost spectra of Fig. 1, but the valence-band spectra show no evidence of Cr at the surface. To determine whether Cr intermixes with the Au overlayer, we measured the integrated Cr derived 3*p* core emission as a function of Au coverage for two different Cr interlayer thicknesses, as shown at the top of Fig. 2. These results show an exponential attenuation of the Cr emission. Comparison with a simple exponential attenuation calculated with an escape depth of 5 Å (dashed line) indicates Si outdiffusion through the interlayer into the Au layer. This Si outdiffusion is quantitatively more important for an interlayer thickness of 2 Å than for an interlayer thickness of 8 Å. There is no evidence of Cr outdiffusion into the Au film.

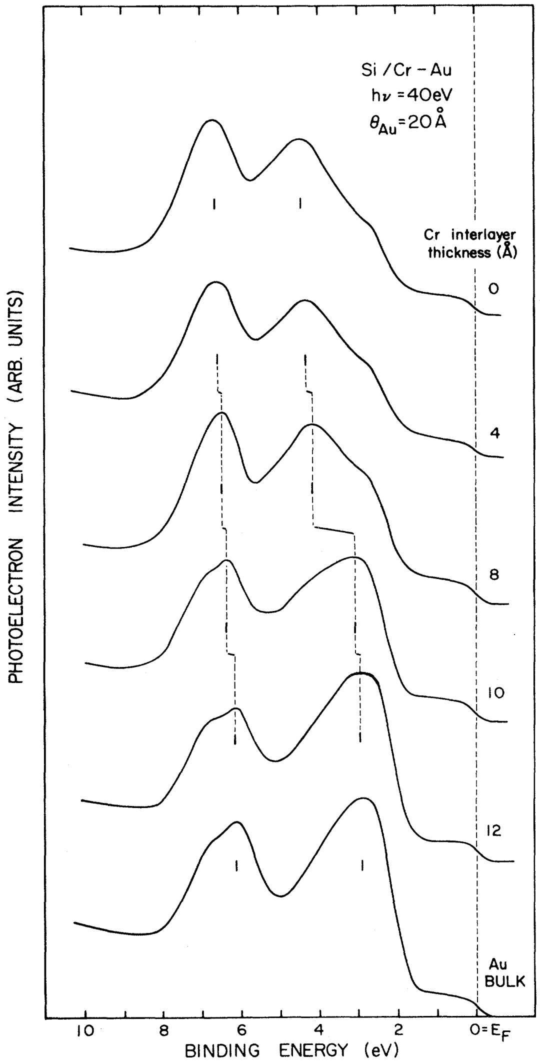

FIG. 1. Valence-band EDC's of the Si-Cr-Au system as a function of the Cr interlayer thickness at a fixed Au coverage of 20 Å. The variation of the energy separation of the Au $5d$ main features (vertical lines) emphasizes the Si-Au intermixing takes place in the presence of the interlayer for Cr coverage below 9 Å but is sharply reduced for higher interlayer thickness.

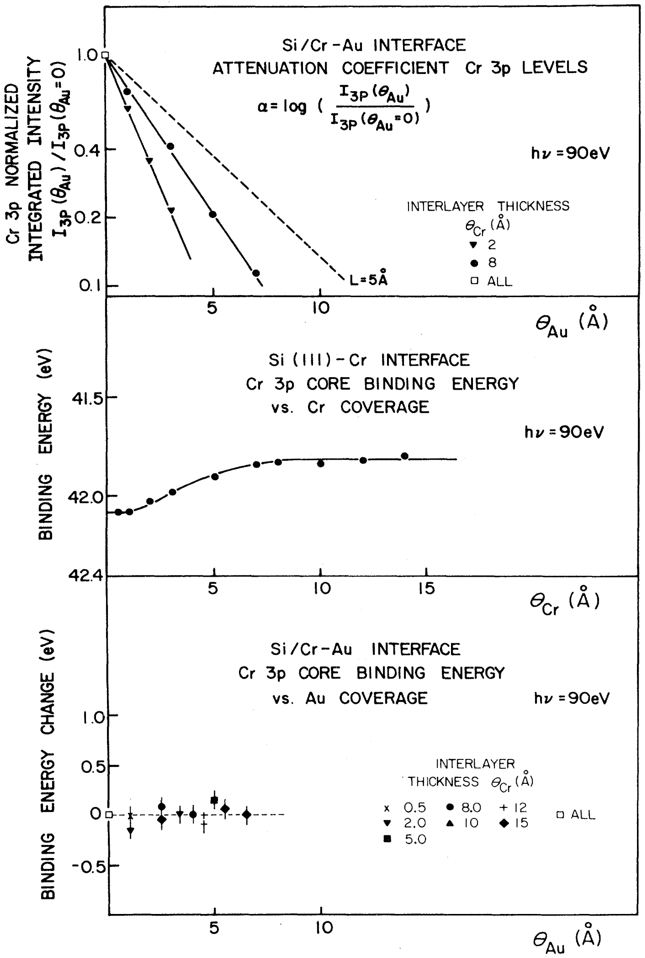

FIG. 2. Top: attenuation coefficient for the integrated emission intensity of the Cr $3p$ cores as a function of Au coverage on the Si-Cr surface. We show experimental data for Cr interlayer thicknesses of 2 and 8 Å. The dashed line represents the theoretical result for exponential attenuation of the $3p$ based on an electron escape depth $L = 5$ Å. Midsection: binding energy of the Cr $3p$ cores as a function of Cr coverage for Cr–Si(111)-(2×1). The Si-Cr reaction corresponds to a chemical shift of ~0.3 eV for the Cr $3p$ cores. Bottom: variation of the $3p$ core binding energy for the Cr atoms in the interlayer as a function of Au coverage. Within experimental uncertainty the average chemical environment of the Cr atoms remains the same after the Si-Au interdiffusion.

In a series of previous papers we showed that the deposition of Cr into the Si(111) surface produces a Si-Cr mixed surface phase of variable composition.[11] When the Si-Cr-Au junction is formed, we now see that Si diffuses into the Au matrix and, in principle, this might imply Si depletion in the Si-Cr region. However, the results shown in Fig. 2 indicate that this is not the case. The Si-Cr reaction which occurs during deposition of Cr on Si(111) produces a chemical shift as large as 0.3 eV for the Cr $3p$ cores (midsection of Fig. 2), but there is no variation of this chemical shift when Au is deposited onto the surface (lowest section). Hence, within experimental uncertainty of ~0.1 eV, the average local chemical environment of Cr atoms in the Si-Cr phase remains the same after the Si-Au interdiffusion. This implies that as Si enters the Au overlayer a corresponding amount must enter the Si-Cr phase to maintain the local stoichiometry. The net results of this diffusion is transport of Si atoms through a stable Si-Cr interface phase.

In Fig. 3 we show very important results which demonstrate that a picture in which the Si-Cr phase acts as a diffusion barrier for atomic interdiffusion of Si and Au is inadequate. By measuring the attenuation of the Si $2p$ core emission as a function of Au overlayer for different Si-Cr interlayer thicknesses, we can show that the attenuation is not proportional to the thickness of the Cr "barrier." In Fig. 3 the emission intensity at a given Au coverage and interlayer thickness is normalized to the initial Si $2p$ emission from the Si-Cr phase. For comparison, results for the Si(111)-Au interface without Cr deposition are also shown (dot-dashed line from Ref. 14). The best representation of

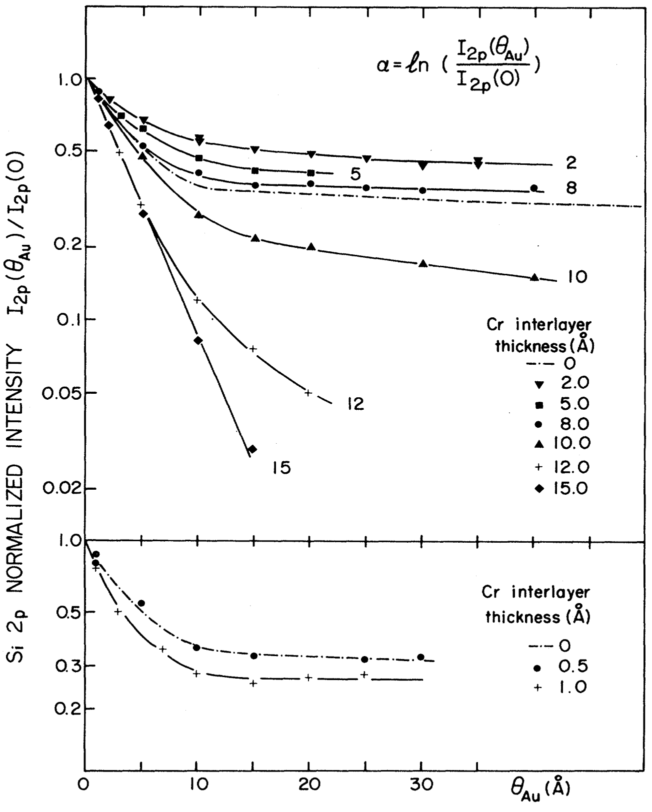

FIG. 3. Attenuation coefficient of the Si $2p$ core emission as a function of Au coverage on the Si-Cr phase. The data show the effect of the presence of the interlayer on Si-Au interdiffusion. The dot-dashed line gives the corresponding result for the Si(111)-Au interface (Ref. 14). For Cr coverage in the monolayer range (lower section), the interlayer slightly reduces Si outdiffusion. For Cr coverages between 2 and 9 Å, the interlayer promotes Si outdiffusion, while for all Cr coverages above 10 monolayers the interlayer sharply reduces the Si-Au reaction.

the *net* effect of the presence of the interlayer on the Si-Au reaction is done by a normalization which takes into account the initial emission from Si surface atoms since this varies with interlayer thickness. Three different ranges of interlayer thickness are clearly evident. First, for Cr coverage of 0–1 Å or monolayer (lower section of Fig. 3), the interlayer weakly affects Si-Au intermixing and reduces Si outdiffusion. Second, for Cr coverages between 1.4 and 9 Å, the interlayer *promotes* Si outdiffusion. Finally, for Cr coverages above 10 monolayers the interlayer *sharply reduces* Si outdiffusion. The maximum promotion effect is obtained at about 2 Å of interlayer thickness, and the trend reverses itself in the monolayer Cr coverage range. Clearly, these results cannot be interpreted with only a simple diffusion barrier model. Hence, there must be a correlation to changes in the local chemistry and energy balance.

In studies of Si(111)-Cr interface formation we suggested[11,18] that there are three formation stages for the Si-Cr interface. In the first ($\theta_{Cr} \lesssim 1$–1.5 monolayers), small core chemical shifts and the relatively rapid attenuation of the substrate emission suggest little or no interdiffusion and weak adatom-substrate interaction ("weak chemisorption"). For $1.5 \lesssim \theta_{Cr} \lesssim 9$–$10$ monolayers, the core levels shift, there is slower attenuation of substrate emission, and the valence states evolve, thus providing evidence of Si-Cr interdiffusion ("reactive interdiffusion"). For $\theta_{Cr} > 10$ monolayers, the Si-Cr reaction is completed and further metal deposition produces an unreacted Cr film on top of the reacted Si-Cr phase ("fully reacted").

The clear one-to-one correspondence between the different stages of Si-Cr interface reaction and the different regimes of catalytic effect of the Cr atoms in the interlayer is compelling and allows us several conclusions. The *promotion* catalytic effect of the interlayer on the Si-Au interdiffusion is related to an increase in reactivity of the Si surface atoms that occur during the reactive interdiffusion stage of the Si-Cr system. The maximum promotion effect occurs just above the onset of the reactive interdiffusion; the interlayer reduces Si outdiffusion below the onset of the Si-Cr reaction. The sharp transition suggests that during the weak chemisorption stage the presence of Cr atoms leaves the energy content of the Si-Si bonds relatively unchanged while the metal atoms "cover up" the ordered surface and act as a thin barrier against the Si-Au interaction. When Cr and Si begin to react, the average Si-Si binding energy is reduced and the broken surface bonds[18] represent sites where the chemically driven Si-Au intermixing may start. The chemically activated character of this interdiffusion process is emphasized by the substantial reduction of intermixing that occurs for interlayer thickness above 9 Å, showing that even very thin layers of *unreacted* Cr on top of the Si-Cr phase act as an effective diffusion barrier for the intermixing.

The gradual reduction in Si outdiffusion that takes place for increasing Cr coverage between 2 and 9 Å is related either to a progressive change of the reactivity of the Si atoms in the Si-Cr phase due to change in bonding character or to the growing importance of a rate-limiting mass transport step in the intermixing process. Discrimination between the two mechanisms will require temperature-dependent studies (to vary the importance of mass transport in limiting the rate of reaction) or procedure whereby the actual concentration profile of Si atoms in the Si-Cr interlayer can be determined. The latter would allow a quantitative correlation of data such as ours with the effective surface concentration of Si atoms and therefore obtain the *specific activity* of the Cr catalyst as a function of interlayer thickness.

In summary, we have shown that interface reaction at the Si-Au junction can be modulated by Cr atoms at the interface, that these Cr atoms can promote or reduce Si outdiffusion from the bulk, and that the nonmonotonic catalytic trend is related to the existence of several nonequivalent microscopic structures for the Si-Cr binary system at the interface. These results point to the importance of investigations of the influence of the interface catalytic effect on the formation of the Schottky barrier because such studies could clarify the relative importance of metal-induced defects and the formation chemistry of the extended interface region in determining the Schottky barrier heights.

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[17] With increasing Si content in Au, the Au atoms become more "atomic," shifting the $5d$ valence states to higher binding energy, decreasing the splitting of the two main $5d$ features toward the atomic spin-orbit value (1.5 eV), and affecting the localized d-d antibonding states so that the sharp d edge of bulk Au 2 eV below E_F is displaced to higher binding energy and only a shoulder is seen in the spectra of reacted Au.

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