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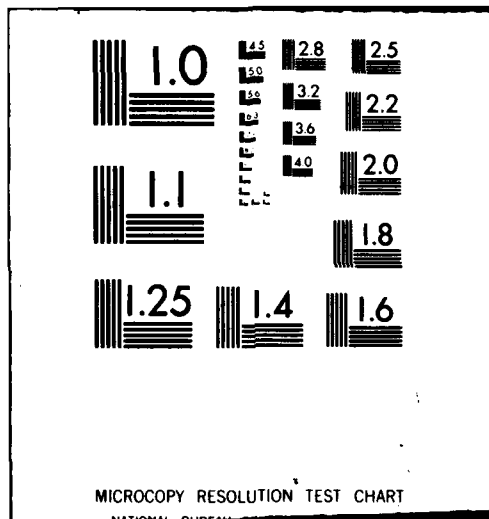
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The Formation of the Schottky Barrier at the V/Si Interface

by

J.G. Clabes, G.W. Rubloff, B. Reihl, R.J. Purtell

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independent of the initial clean surface structure. Formation of the bulk V metal band structure is not complete until $\sim 30\text{-}40$ A V coverage, indicating coverage-dependent structural effects in the growth of the metal film. These effects also seem to produce secondary influences on ϕ_{bn} with higher coverage or mild ($\sim 200^\circ\text{C}$) annealing. However, upon higher temperature annealing ($< 350^\circ\text{C}$) the trend reverses, with ϕ_{bn} decreasing to a value ($\sim 0.64\text{eV}$) characteristic of the bulk VSi_2 contact which is formed at $500\text{-}550^\circ\text{C}$; this change in the behavior of ϕ_{bn} is directly correlated with the onset of atomic mixing across the interface.

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The Formation of the Schottky Barrier at the V/Si Interface*

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ABSTRACT

Synchrotron radiation photoemission measurements have been used to study the behavior of the Schottky barrier height ϕ_{bn} and electronic structure of the V/Si interface for both cleaved Si(111)-(2 $\times$ 1) and sputter-cleaned Si(111)-(7 $\times$ 7) surfaces. Although the Schottky barrier height ϕ_{bn} of the clean surface is influenced by surface reconstruction (and by steps), the barrier becomes pinned at low ($\sim 2 \text{ \AA}$) V coverage at a position essentially independent of the initial clean surface structure. Formation of the bulk V metal band structure is not complete until $\sim 30\text{-}40 \text{ \AA}$ V coverage, indicating coverage-dependent structural effects in the growth of the metal film. These effects also seem to produce secondary influences on ϕ_{bn} , which are manifested as a gradual increase of ϕ_{bn} with higher coverage or mild ($\sim 200^\circ\text{C}$) annealing. However, upon higher temperature annealing ($\geq 350^\circ\text{C}$) the trend reverses, with ϕ_{bn} decreasing to a value ($\sim 0.64 \text{ eV}$) characteristic of the bulk VSi₂ contact which is formed at $500\text{-}550^\circ\text{C}$; this change in the behavior of ϕ_{bn} is directly correlated with the onset of atomic mixing across the interface.



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To achieve a basic understanding of what mechanisms determine the Schottky barrier height of the metal/Si interface, it is necessary to establish correlations between the electrical characteristics of the contact and other properties such as interface electronic structure, composition, and microstructure. Over the past few years, a number of investigations have revealed important aspects of the overall interface behavior, particularly for near-noble metals which form silicide compounds.¹⁻⁵ These studies have also shown specific chemical and electronic mechanisms which might determine the Fermi level pinning position, including specific interface chemical bonds^{6,7} and metal impurities in the Si lattice⁸. However, these studies have not clarified the relation of such behavior to the interface electrical properties.

Recent surface spectroscopy studies have identified the chemistry which occurs at the refractory-metal/Si interface.^{9,10,11} With this information available, we have undertaken synchrotron radiation studies of core-level/band-bending shifts during Schottky barrier formation at low metal coverage¹² to assess which interface characteristics influence the Schottky barrier height ϕ_{bn} . These initial investigations already suggest how ϕ_{bn} is affected by interface microstructure and electronic structure and by the progress of the silicide formation reaction.

Synchrotron radiation from the 240 MeV Tantalus-I electron storage ring at the University of Wisconsin-Madison was used with a UHV toroidal grating monochromator and a display-type electron spectrometer¹³ to measure angle-integrated $h\nu$ -dependent photoemission spectra for the V/Si(111) interface. The total instrumental energy resolution was ≤ 0.2 eV. The Si(2p) core levels were measured with a resolution ~ 150 meV, so that core level shifts (and thereby changes in ϕ_{bn}) as small as ~ 10 meV could be detected. Interface chemical bonding and electronic structure were observed in valence band spectra at various $h\nu$, while the metal-induced changes in Si band-bending or Schottky barrier height were determined from shifts in the substrate Si(2p) core level binding energy.¹² The Si samples were prepared by either (i) cleavage at room temperature (using p-Si samples), which gives the metastable

(2×1) surface reconstruction, or (ii) Ar⁺ ion bombardment and thermal annealing (using n-Si wafer samples 0.010" thick), which produces the stable (7×7) reconstruction. Thin V overlayers (1-15 Å) were deposited at room temperature by direct sublimation from a resistively-heated V wire, with coverage determined by a quartz crystal thickness monitor. For the Si(111)-(7×7) wafer samples, annealing was carried out by direct resistive heating of the sample, and the annealing temperature was determined with an infrared pyrometer.

The valence band photoemission spectra, shown for $h\nu = 21$ eV in Fig. 1, demonstrate the changes in interface electronic structure which occur upon deposition of thin V layers. The spectrum for the clean cleaved Si(111)-(2×1) surface shows a strong intrinsic surface state at ~ -0.9 eV¹⁴. Although the surface states are fully quenched upon deposition of 1 Å V, the metallic character of the overlayer film is not developed until ~ 4 Å V coverage, when the Fermi-Dirac cutoff lineshape appears at the Fermi energy E_F . The non-metallic character of the surface at low coverage suggests that the chemical bonding between V and Si in this range is essentially like atomic chemisorption rather than the metallic band formation observed at higher coverage. The coverage-dependence of the Auger line intensities¹⁵ indicates that formation of 3-dimensional islands on the surface is unlikely.

More detailed valence band studies¹⁵ show that, in contrast to the behavior for near-noble metals, silicide formation does not occur at room temperature even at very low coverage. Furthermore, the final V metal bulk band structure, seen in Fig. 1 for 75 Å V, is not established until $\sim 30-40$ Å coverage. This slow evolution of the metal band structure may represent the growth of a metal film which is homogeneous overall but has coverage-dependent changes in its atomic structure. Although the specific nature of these structural changes is not known at present, they might include, e.g., conversion of an initially amorphous layer to a polycrystalline state or longer range microstructural effects such as changes in grain size or strain.

The Si(2p) core level spectrum has been measured using two different photon energies. At $h\nu = 120$ eV the escape depth of the photoexcited core electrons is ~ 5 Å (surface-sensitive mode), while for $h\nu = 108$ eV the escape depth is ~ 13 Å (bulk-sensitive mode) and provides a better monitor of metal-induced band-bending changes in the underlying Si substrate. As seen in the surface-sensitive mode, the Si(2p) core level peaks broaden with metal coverage, indicating electronic interaction between the Si surface atoms and the deposited V atoms, while the shape of the bulk-sensitive spectrum is basically unchanged.

We concentrate here on the changes in the (n-type) Schottky barrier height $\phi_{bn} = E_C - E_F$, where E_C and E_F refer respectively to the energies of the Si conduction band minimum and the Fermi level at the interface. Since band-bending in the Si shifts the entire Si band structure at the interface (including core levels and valence and conduction band edges) rigidly up or down together, changes in ϕ_{bn} can be directly monitored from changes in the Si(2p) core level binding energy. In the bulk-sensitive mode, changes as small as ~ 10 meV can be detected. The barrier height for the clean cleaved Si(111)-(2×1) surface (0.79 eV)¹⁶ is used as the reference point for converting core level binding energies to ϕ_{bn} 's.

The Schottky barrier heights for the clean Si surfaces and for thin V layers deposited on Si at room temperature are shown in Fig. 2. For these measurements, which involved either fresh cleaves or sample transfer to the evaporation position and subsequent realignment, we estimate the reproducibility as $\sim \pm 20$ meV. For four measurements on the clean cleaved Si(111)-(2×1) surfaces, three different ϕ_{bn} values were obtained. We take the lowest binding energy (largest ϕ_{bn} value) as the reference point $\phi_{bn} = 0.79$ eV for the "ideal" cleaved surface because: (i) it gives the separation $\phi_{bn}(2\times 1) - \phi_{bn}(7\times 7) = 180$ meV in agreement with previous work¹⁷; (ii) it was obtained twice; and (iii) for these cleaves a sharp (2×1) LEED pattern was observed, while for the other two cleaves the LEED pattern showed streaked half-order spots and splitting of the integral order spots in one direction, indicating a relatively high density of atomic steps on the surface. Thus these differences in surface

microstructure seem to influence the clean surface barrier height considerably. In contrast, these structural differences appear not to significantly alter the overall surface electronic structure: for all these cleaves, sharp intrinsic surface states were observed at the same energy position.

Starting from the "ideal" cleaved (2×1) surface, ϕ_{bn} decreases sharply with the first 1-2 Å V coverage to ~ 0.67 eV. Although ϕ_{bn} for the sputter-cleaned (7×7) surface begins at a considerably lower value (~ 0.61 eV) than that of the clean (2×1) surface, upon deposition of ~ 2 Å V it rises to about the same ϕ_{bn} value (~ 0.67 eV) as observed for a similar V coverage on the (2×1) surface. This demonstrates that the different initial Fermi level pinning conditions of the clean surface have been overcome and that metal-induced electronic states associated with the V-Si bonding now determine the Fermi level position at the interface.

After its initial sharp decrease on the (2×1) surface, ϕ_{bn} then rises more slowly with higher V coverage. This increase may be related to the coverage-dependent atomic structure changes of the V overlayer inferred above from the valence band photoemission spectra. If this is so, the different ϕ_{bn} 's attained on the two (2×1) cleaved surfaces (e.g. at 4 Å V) may indicate that the metal film growth proceeded somewhat differently on these two surfaces. Although it is interesting and perhaps significant that the barrier height is changed at higher coverage, these appear to be more complicated secondary effects compared to the initial Fermi level pinning associated with the basic V-Si bonding produced at lower coverage.

The dependence of the Schottky barrier height on the state of interfacial reaction is shown in Fig. 3 for the sputter-cleaned Si(111)- (7×7) surface. Starting from ϕ_{bn} for the 25°C deposition, the reproducibility of ϕ_{bn} was better (± 10 meV) than before since the annealing could be done in the measurement position without moving the sample.

Upon annealing to 200°C, ϕ_{bn} increases further to ~ 0.70 eV, a trend like that seen for higher coverage at 25°C (Fig. 2). At higher annealing temperatures, the trend clearly reverses

and ϕ_{bn} decreases markedly, essentially reaching a saturation value ~ 0.64 eV already at 350°C . Other investigations^{11,15} have established that atomic mixing across the V/Si interface does not occur at 200°C but begins at 350°C , while formation of the bulk silicide (VSi_2) contact does not take place until 500°C . Therefore, we conclude that the behavior (qualitative as well as quantitative) of ϕ_{bn} is dramatically influenced by strong interfacial reaction (atomic mixing). This interface chemical process at 350°C already pins ϕ_{bn} at essentially the final value observed for VSi_2 formation at 500°C . Finally, we note that this Schottky barrier height agrees well with that determined from I-V characteristics of much thicker VSi_2 Schottky diodes produced under standard thin film conditions.¹⁸

These synchrotron radiation studies provide a valuable tool for determining ϕ_{bn} with high resolution (compared to the range of barrier heights observed from different metal/Si contacts) during the important initial stages of interface formation which determine the Fermi level pinning position of the final metal contact. Furthermore, such measurements of ϕ_{bn} can be correlated with the interface electronic structure and chemical reactivity which are simultaneously observed in these investigations.

Our findings can be summarized in the following way. The clean Si Fermi level position is clearly influenced by reconstruction of and steps on the surface. However, a thin metal overlayer ($\sim 1\text{-}2$ Å) pins the Schottky barrier height at a position which seems to be associated with the basic V-Si bonding at the interface, independent of the initial clean surface structural conditions. This thin metal layer has not yet developed full metallic character. Our results also indicate that changes in the atomic structure of the unreacted V film with coverage influence the electronic structure, and they provide a secondary influence on ϕ_{bn} . Finally, the qualitative as well as quantitative behavior of the Schottky barrier height is strongly altered by interface chemical reactions which involve atomic mixing across the initially unreacted metal/Si interface.

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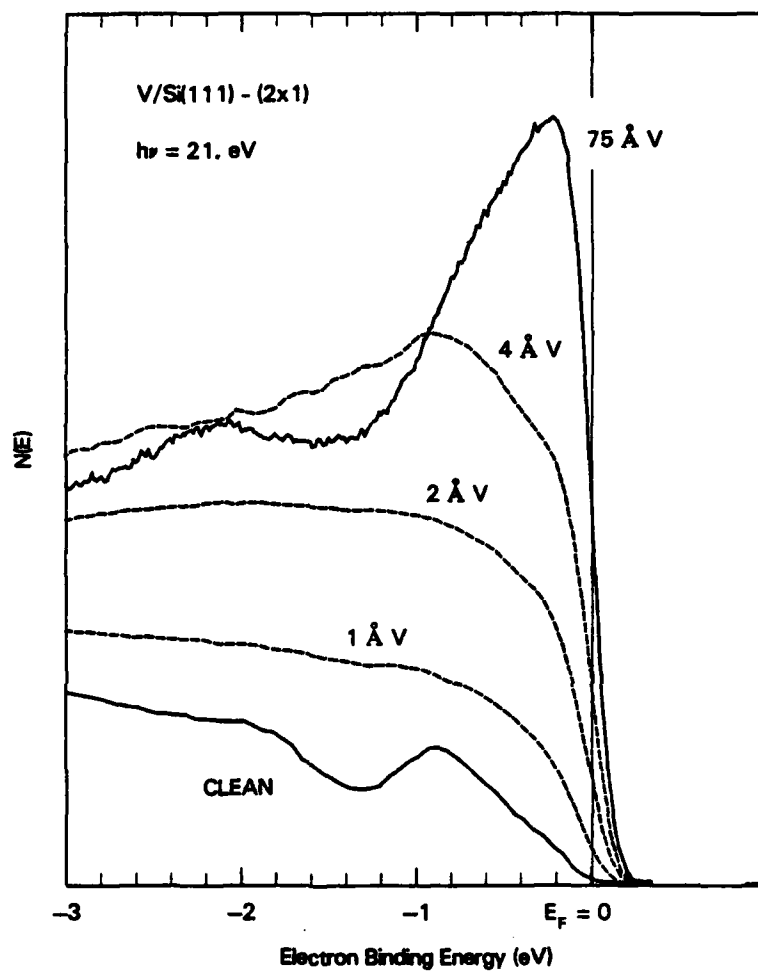


Fig. 1. UPS ($h\nu = 21. \text{ eV}$) valence band spectra for the clean cleaved Si(111)-(2x1) surface and for V deposited at room temperature.

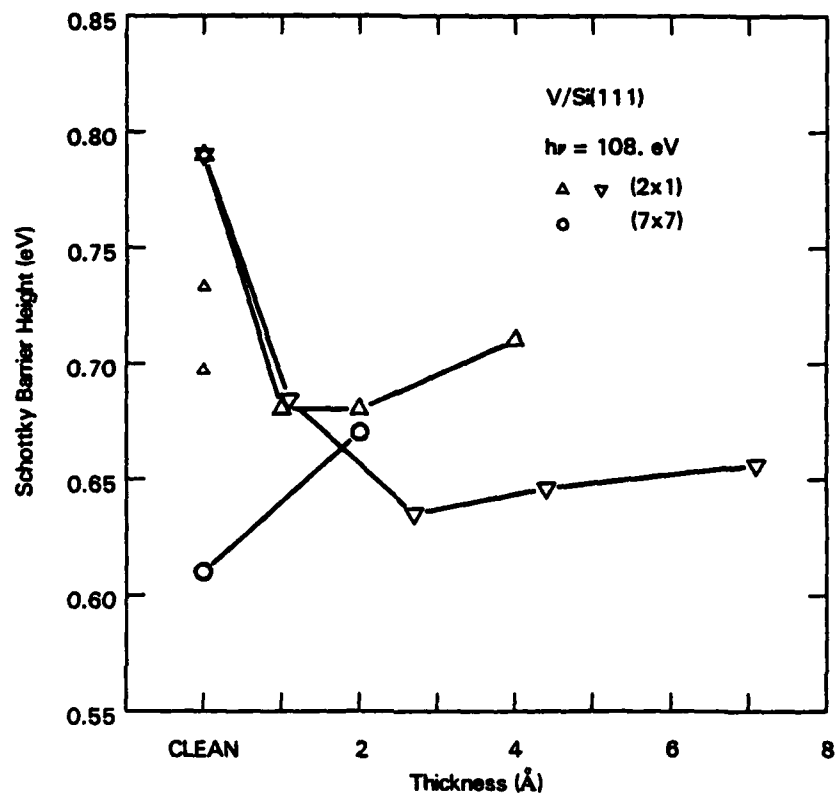


Fig. 2. Schottky barrier height ϕ_{bn} for clean Si(111)-(2 $\times$ 1) and Si(111)-(7 $\times$ 7) surfaces and for thin V overlayers deposited at room temperature, as obtained from the Si(2p) core level binding energy in the bulk-sensitive ($h\nu = 108. \text{ eV}$) mode.

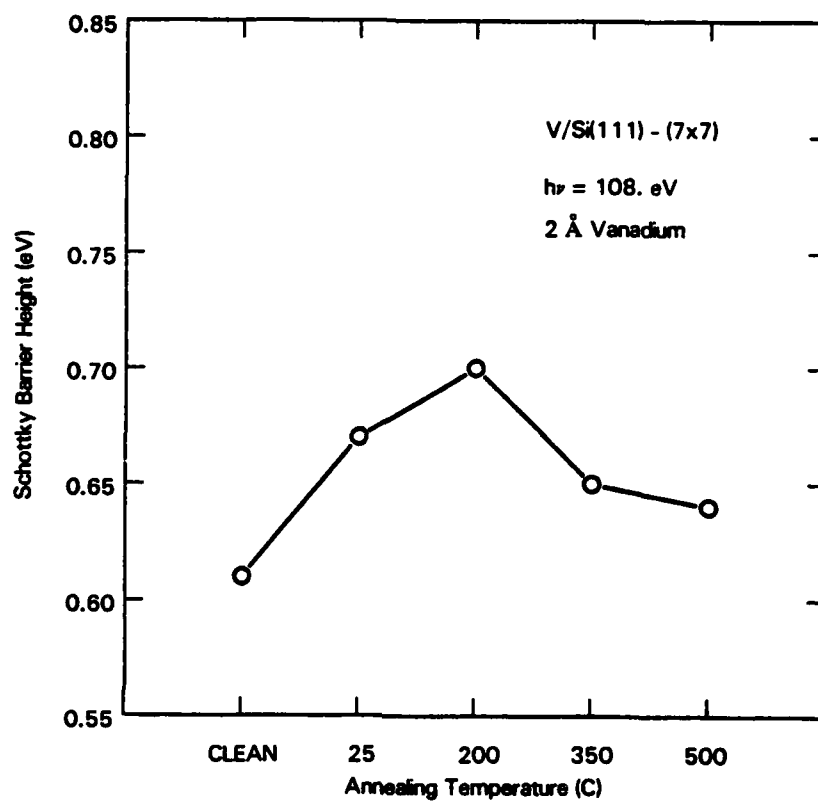


Fig. 3. Schottky barrier height ϕ_{bn} for annealing of 2 Å V film deposited on the clean Si(111)-(7x7) surface, as obtained from the Si(2p) core level binding energy in the bulk-sensitive ($h\nu = 108. \text{ eV}$) mode.

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