Considerable efforts have recently been devoted to basic studies of metal/semiconductor interfaces because the mechanism responsible for Schottky barrier formation remains unexplained and because new experimental tools (e.g. surface spectroscopies, channeling) can now give more direct information about interface properties. Current and anticipated applications of such interfaces in microelectronic devices provide a strong practical significance to such studies, especially for transition metal/Si interfaces. Recent studies have already revealed important aspects of the microscopic chemistry, electronic properties, and microstructure at near-noble metal/Si interfaces, where silicide formation plays a dominant role. We report here preliminary results of our studies of the refractory metal/Si interfaces V/Si(111) and V/Si(100).

The V/Si interface is known to have a low Schottky barrier height (20.53 eV) for n-Si, and under fairly clean conditions only one silicide phase, VSi2, is formed at ~500–600 °C. Under some conditions, the growth rate of VSi2 is linear in time, suggesting an interface-controlled reaction. In some cases, e.g., oxygen contamination or a damaged or amorphous silicon substrate, formation of metal-rich silicides V5Si and V5Si4 has been observed.

We discuss here results for V on Si(111) and Si(100) surfaces studied by ultraviolet (UPS) and x-ray (XPS) photoemission spectroscopies and by Auger electron spectroscopy (AES) under ultrahigh vacuum conditions. The samples were cleaned by Ar+ sputtering and annealing. Vanadium was deposited by direct sublimation from a pure V wire. In the UPS spectra a marked increase in emission is observed just below the Fermi energy, EF, upon V deposition. At ~20 Å V coverage the UPS spectrum is dominated by occupied V(3d) band states from ~0.8 eV to EF, while emission from the Si substrate is not detectable. In the AES spectrum the intensity of the Si LVV line decreases monotonically with V coverage, except for modifications in the loss spectrum on the lower energy side of the structure its shape does not change significantly. The XPS spectra for Si and V core levels show the expected intensity behavior while no chemical shifts greater than 0.2 eV are observed. UPS incremental difference curves at very low coverage (0.25–0.5 Å coverage increments) show essentially the same spectral features as thicker films. Heat treatments of a ~20 Å V film to about 200 °C for several minutes do not change the UPS, XPS, or AES spectra. All these observations suggest strongly that no compound formation or intermixing occurs at room temperature.

Upon annealing such a film for a few minutes at ~530 °C (well below the VSi2 formation temperature), the spectra change considerably and reveal strong V–Si intermixing in the overlayer. The V concentration in the initial metal film decreases by about 40%, as seen by the intensities of the V(3d) band in UPS, the V core levels in XPS, and the V AES lines. In addition, the fine structure in the UPS spectrum changes, although the dominant V(3d) emission remains near EF as in V metal. The UPS spectrum does not show any clear agreement with that obtained for VSi. The Si XPS core levels and AES lines appear and grow to about 40% of those for elemental Si. Additional 350 °C annealing cycles of comparable time do not further alter the spectra. We conclude that a mixed V–Si film has formed upon 350 °C annealing, with an overall V/Si ratio of 3:2. TEM studies are in progress to determine whether this represents a well-defined compound phase.

Further annealing to 500 °C for a few minutes causes formation of the expected final silicide product, VSi2, as confirmed by TEM phase analysis of the overlayer film. This changes the UPS spectrum dramatically, producing prominent new features located at about ~1.8, ~4.0, ~6.0, and ~7.5 eV. This observation is in good agreement with recent UPS studies of clean VSi2 crystals fractured in situ. The shape of the Si LVV Auger spectrum for VSi2 is very similar to that for elemental Si, in contrast to the behavior of the near-noble metal silicides. The relative intensities of the Si LVV and V LMM AES lines and the Si and V XPS core levels also support a stoichiometry ~VSi2. This composition remains stable over a fairly large temperature range, from ~500 °C to ~650 °C. At higher temperatures V diffuses into the Si bulk.

Silicide formation at this refractory metal/Si interface differs in several interesting aspects from that at the near-noble metal/Si interfaces. First, reaction at low temperatures (≤200 °C) does not occur; in fact, the first silicide compound phase expected does not appear until ~500 °C. Second, silicide formation under these atomically clean conditions does not occur at temperatures lower than that required under standard thin film growth conditions, although for the near-noble metal silicides the clean conditions reduced silicide formation temperatures considerably.

The strong V–Si intermixing observed upon 350 °C annealing is surprising because standard thin film studies have shown that silicide phases more metal-rich than VSi2 are not formed under even moderately clean, ordered interface conditions and that other phases (V2Si, V5Si4) are not pro-
duced when VSi$_2$ can be formed. If the V–Si mixture we observe after 350°C annealing is a well-defined silicide compound, the present results would represent qualitatively new behavior at the V/Si interface. Alternatively, if the mixture is not a well-defined compound, this would mean that strongly interdiffused material is created as a precursor to silicide formation, which has not been seen for near-noble metal silicide formation.

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10) Y. Nono, P. G. Himpel, and D. E. Eastman (to be published).


Summary Abstract: Site-specific densities of states for cleaved and sputtered GaAs (110) from Auger line shapes$^{a,b}$

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The nature and extent of interfacial chemical reactions are major factors affecting the electronic properties of semiconductor–metal or semiconductor–semiconductor interfaces. These reactions and the resulting chemical phases may depend strongly on the surface structure and the extent and nature of structural defects. A first step to understanding defect-related chemical phase formation and interfaces is to correlate local chemical properties with structural defects. We have made an initial attempt to do this for GaAs (110) by comparing the results of several techniques. We have examined the cleaved and sputtered GaAs (110) surface with X-ray photoemission spectroscopy (XPS), Auger electron spectroscopy (AES) line shape analysis, low-energy electron diffraction (LEED), and scanning electron microscopy (SEM).

In the Auger process, because the initial core hole is localized around one atom, the probability of exciting a valence electron in a core–core–valence transition falls off quite rapidly away from the core. Consequently, the charge distribution that is probed by such transitions is site-specific and may differ if the initial core hole is made on the anion or the cation. This is in contrast to a photoemission measurement, where sites widely separated in R may contribute to the photoelectron intensity at a particular value of energy.

Auger and XPS measurements are made with standard instrumentation. In order to extract true intensity distributions, both the Auger and XPS measurements are deconvoluted with an instrument/bias function to correct for (1) the analyzer broadening, and (2) the inelastic scattering of the electrons as they traverse the solid. Additionally, a Lorentzian or a sum of Lorentzians is included in the deconvolution to correct for the broadening and satellite lines in the XPS data resulting from the achromatism of the X-ray source, and for the broadening in the Auger data resulting from the lifetime of the core levels involved in the transition.

LEED and SEM measurements were made on the cleaved and sputtered GaAs (110) surface. LEED data were recorded with an on-line vidicon camera. SEM measurements were made in a standard SEM with a field emission source.

Changes in both the Auger line shapes and in the XPS valence band spectrum are evident with sputtering. On the basis of the Auger data, the scanning electron micrographs of these changes can be explained by a surface enrichment in