Schottky-Barrier Formation at Single-Crystal Metal-Semiconductor Interfaces

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Electrical behaviors at two single-crystal metal-semiconductor interfaces are studied. Schottky-barrier heights of $NiSi_2$ layers grown under ultrahigh-vacuum conditions on n-type Si(111) are found to be 0.65 and 0.79 eV for type-A and type-B epitaxial systems, respectively. These results are compared with the proposed theoretical models of Schottky barriers.

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The formation of Schottky barriers (SB) at metal-semiconductor interfaces has attracted much attention for over thirty years.[1-3] Various models were proposed to explain how these rectifying barriers are determined. But thus far no theory emerges which gives explicit account of the experimental results. The details of the structure, impurity, stoichiometry, defects, etc., at the metal-semiconductor interface are not known in most studies, making progress in this field difficult. In the very few cases where careful characterization of the interface was made, the structure was too complicated because of polycrystallinity to provide a reasonable basis for a first-principle calculation. With a few exceptions, almost all metal films grown on semiconductor are multicrystalline. A homogeneous interface, of known atomic structure, between a single-crystal metal and a single-crystal semiconductor is an ideal system for detailed theoretical investigation. In this Letter, measurements of Schottky-barrier height (SBH) are presented for just such a system.

Thin films of single-crystal $NiSi_2$ and $CoSi_2$ can be grown with very high degree of perfection on silicon under ultrahigh-vacuum (UHV) conditions.[4] Single-crystal Al films[5,6] can also be grown on differently reconstructed GaAs(100) surfaces, but the structures at such interfaces are largely unknown. The $NiSi_2Si$ epitaxy is quite unique in that uniform and continuous single-crystal metal layers can be grown on Si(111) and (100). Moreover, the orientation of the $NiSi_2$ films grown on Si(111) can be controlled to be either identical to that of the substrate (type-A orientation), or to be rotated 180° about the surface-normal direction with respect to the substrate (type-B orientation).[7,8] Lattice imaging of such silicide-silicon interfaces by high-resolution transmission-electron microscopy (TEM) has demonstrated the sharpness of the interface and revealed the most likely interfacial atomic structure.[9,10] In this Letter, electrical properties of type-A and type-B $NiSi_2Si(111)$ junctions are determined. It is shown that SBH is higher for the type-B interface by 0.14 eV over that of type A. Such a large difference is not expected on the basis of previous SBH results obtained largely from polycrystalline metal films. This shows the importance of having well-characterized, homogeneous interfaces as an experimental basis for understanding the SB formation mechanism(s).

Arrays of circular windows with diameters of 127–508 μm are photolithographically defined in the 3000–5000-Å-thick SiO_2 layer grown on n-type Si(111) wafers. Also interspersed on the patterned wafers are 3-mm-wide stripe openings for better characterization by low-energy electron diffraction (LEED), Auger-electron spectroscopy, Rutherford backscattering spectroscopy (RBS) and channeling, TEM, etc. Samples are degreased and exposed to HF fume for ~ 5 sec to remove oxide in the windows, and rinsed with methanol. They are cleaned by a heat treatment (1000 °C for 2 min) in a UHV chamber with base pressure of 1×10^{-10} Torr. The exposed Si region displays a good 7×7 LEED pattern even though a small amount of carbon is detected by Auger analysis. Thin (60–70 Å thick) single-crystal $NiSi_2$ template layers are then grown in exposed Si regions by deposition of Ni and annealing to 500 °C.[7] The orientation (A or B) of such layers is controlled by varying the initial coverage of deposited Ni. Silicon deposition is used in conjunction with Ni deposition in the growth of some type-B templates.[10] Thick (700–1000 Å) $NiSi_2$ type-A and type-B layers are grown by deposition of nickel onto the template layer of the corresponding orientation while the sample temperature is kept at $\sim 700-750$ °C.[8] The orientation of these silicide layers is determined by LEED and RBS and channeling. The perfection of these single-crystal layers has already been described.[10] The unreacted Ni on top of the SiO_2 is removed by a chemical etch. Ohmic contact is made to the back side of the sample without heat-

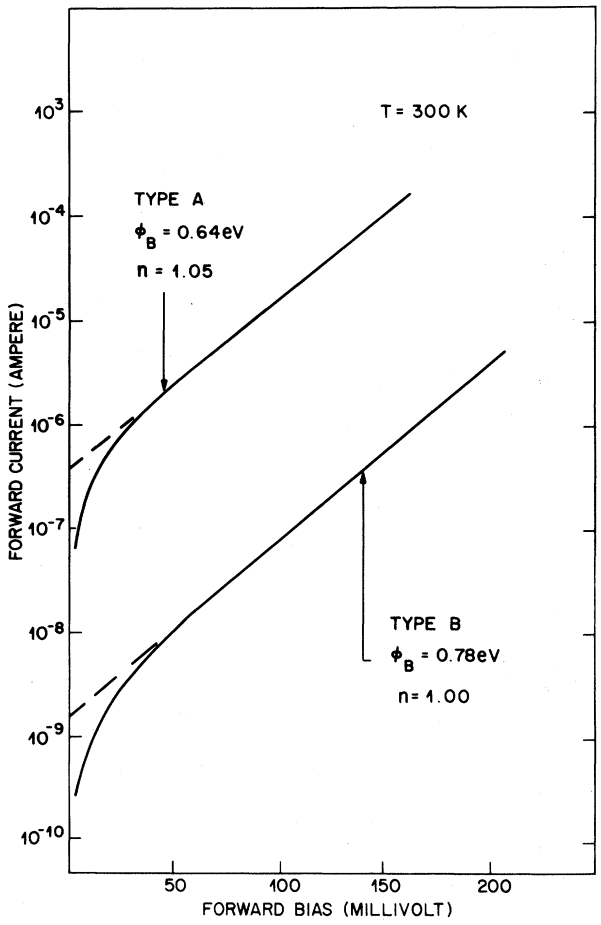

FIG. 1. Forward current characteristics of thin (~ 70 Å) type-A and type-B $NiSi_2$ layers on Si(111). Spot size is 394 μm.

ing the sample above room temperature, by antimony deposition, pulsed-laser melting of Sb and surface Si, and aluminum deposition. SBH's are determined[11] by current-voltage (I-V) and capacitance-voltage (C-V) scans on an x-y recorder. Metallized openings are probed with thin gold wire to avoid puncturing the thin layers.

Forward current characteristics of a type-A and a type-B template layers are shown in Fig. 1. These data are for junctions which show close to ideal electrical behaviors, approximately 50% of the samples studied. All dots which show a linear dependence of log I on V always display good ideality factor (< 1.06) and extrapolate to yield the same barrier height (± 0.01 eV) of the corresponding orientation. Capacitances are measured mainly at 1 MHz; a few select samples are studied with different frequencies ranging from 20 kHz to 2 MHz. Linear C^{-2} dependence on V is found for almost all diodes studied, with the slope agreeing well with the nominal doping concentration. For a given orientation, extrapolations consistently yield the same SBH as obtained by the I-V method. Results of these electrical measurements are summarized in Table I. Thick (700-1000 Å) and thin (~70 Å) junctions of the same orientation yield the same SBH (± 0.01 eV); this demonstrates that misfit dislocations which exist at the interfaces of the thick layers (~10^5 per cm^2), but not at the thin pseudomorphic template layer interfaces,[10] do not contribute actively to the formation of SBH. Recently published results[12] suggest that misfit dislocations may pin

TABLE I. Schottky-barrier heights of UHV grown $NiSi_2$ single crystals to n-type Si(111).

Orientation	Film thickness (Å)	Formation temperature (°C)	Misfit dislocations	SBH (eV) [a] I-V [b]	C-V [c]
B	~70	500	no	0.79	0.79
A	~70	500	no	0.65	0.65
B	700–1000	750	yes	0.78	0.79
A	700–1000	750	yes	0.65	0.65

[a]Tabulated values are the intrinsic barrier heights (flat bands) with no Schottky lowering. The experimental error of every entry is estimated to be 0.01 eV.

[b]Only junctions with ideality factor of less than 1.06 and linear semilogarithmic behavior over two decades are included. The effective Richardson's constant is 100 A cm^{-2} K^{-2}. Schottky lowerings of 18 to 30 mV are added.

[c]Obtained from over 150 different spots on 6×10^{15} cm^{-3} P and 3×10^{16} cm^{-3} As substrates.

the Fermi level at semiconductor interfaces.

SBH's of metal silicides to Si were previously reported to be nearly constant for a given metal, independent of the structure and stoichiometry of the silicides.[13,14] For instance, Ni_2Si, NiSi, and $NiSi_2$ all have the same SBH, 0.66 ± 0.02 eV, on n-type (111) and (100) substrates. This has led to speculations of an interfacial layer, interstitial metal atoms, or Si vacancies being responsible for the SBH to Si. With the present results, a change in viewpoint is suggested.

The difference between SBH's of types A and B is rather significant considering the subtle difference between the atomic structures at the two interfaces. Atomic structures of the two sevenfold coordinated interfaces are depicted in Fig. 2. Computer simulations based on these unrelaxed structures agree well with high-resolution TEM images.[10] The structures of these two interfaces are very similar, differing only in the positions of the third- and higher-nearest neighbors to the last nickel layer. The key feature is the unpaired electrons which because of Ni-Si hybridization are directional,[15] similar to dangling bonds.

Beside the original Schottky description, there are two models proposed to account for how the Fermi level arrives at its value at the interface. One involves the filling of the surface/interface states,[16,17] and the other depends on local chemical bonding[18] and/or the formation of defects.[19,20] No experimental results are known regarding the electronic structure of the A and the B interfaces. Self-consistent calculations are being performed because the most straightforward explanation for the difference in SBH is the existence of electronic states positioned higher in the band gap for type A than for type B. Such calculations may have to include atomic relaxations which may exist at the interfaces but are outside the TEM resolution. An alternative explanation due to Tersoff[21] suggests that the difference in SBH may be due to electronic properties characteristic of hexagonal Si (a lower conduction-band minimum) at the type-B interface. Defects 3 Å away from the interface should have identical energy levels for the A and the B and hence cannot account for the present results. I am not aware of any defect sites right at the interface which would give rise to energy levels differing by 0.14 eV. High-resolution TEM[10] does not show any evidence of point defects of the high density[22] required for Fermi-level pinning.

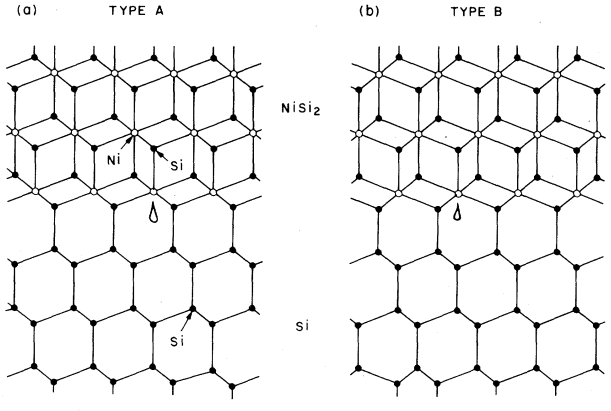

FIG. 2. Balls and sticks models of the two $NiSi_2$-Si(111) interfaces viewed in the $\langle 1\bar{1}0 \rangle$ direction. Orbitals of unpaired electrons are also indicated.

The published $NiSi_2$ SBH to n-type Si(111) is 0.64–0.7 eV for non-UHV-grown layers.[14,23,24] Electron microscopy has shown such layers to have both type-A and type-B grains.[25] An interface which consists of regions of high barrier and regions of low barrier would display electrical behavior intermediate between the two, but more closely resembling the lower barrier. So it can be argued that 0.65 and 0.79 eV are the barrier heights associated with type-A and type-B interfaces, respectively, and that the reported SBH of non-UHV films is the result of polycrystallinity. However, the SBH of type-A $NiSi_2$ (0.65 eV) is close to the 0.66 eV usually associated with polycrystalline Ni silicides (Ni_2Si, NiSi, and $NiSi_2$).[14] This suggests that if the observed SBH insensitivity to stoichiometry, structure, etc., is due to some particular mechanism, other than simple averaging from polycrystallinity, then this mechanism may also be in effect at type-A $NiSi_2$ interface. The existence of a thin type-A $NiSi_2$ layer at every (Ni_2Si and NiSi) interface can almost be ruled out on the basis of TEM[25] and the fact that there is no such equivalent layer at a (100) interface.[26] If this mechanism is defects, then the type-A $NiSi_2$ interface may also have these defects. The SBH of the type-B interface would then be determined by a different mechanism, most likely by the intrinsic electronic states. There is evidence that type B has lower interfacial energy than type A, because $NiSi_2$ will crystallize overwhelmingly in the B phase upon pulsed laser melting and rapid recrystallization.[27] So one can even argue that the type-B interface is more stable and hence has a negligible density of defects; it is a known fact that they have very low density of steps.[10]

Many research efforts have been directed at

the understanding of phenomena occurring at the metal-semiconductor interfaces. Understanding the formation of the SBH on a fundamental basis still remains the most challenging problem. With the discovery of the stabilization of ultrathin $NiSi_2$-Si epitaxy under UHV conditions, sharp and homogeneous metal-semiconductor interfaces are now available. At the $NiSi_2Si(111)$ interface, either of the two "double position" orientations, perfect in its own right, can be singled out and studied separately, providing a new variable and a unique comparison. Moreover, the interface structure has already been determined. Thus, this is an ideal system to better our understanding of the SB. We have performed the first measurement of barrier height formed by a single-crystal metal on silicon. Experimental results indicate the importance of crystallographic orientation and, hence, the interface structure.[26] This dependence suggests an intrinsic SB mechanism; however, defects associated with only one interface cannot be ruled out.

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[26]Preliminary results (R. T. Tung, to be published) show that the SBH of single-crystal $NiSi_2$ on Si(100) differs significantly from that of either of the two $NiSi_2$/Si(111) interfaces. This again points to the importance of interfacial structure in the SB formation.

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