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States at epitaxial $NiSi_2$/Si heterojunctions studied by deep-level transient spectroscopy and hydrogenation

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We have explored the possible role of bulk and interface defects in determining the potential barrier occurring at an "ideal" epitaxial metal-semiconductor contact. The results of deep-level transient spectroscopy, current-voltage, and capacitance-voltage measurements before and after hydrogenation of the samples show little evidence for the presence of defects. These observations are consistent with the idea of an intrinsic mechanism for Schottky-barrier formation. We also demonstrate that under certain substrate preparation conditions boron may be unintentionally introduced into the surface region.

A long-standing and still unsolved problem in solid-state physics concerns the microscopic origins of the potential barrier occurring at a metal-semiconductor contact. Historically, the reasons for this are twofold. First, theoreticians have not yet been able to describe adequately the interface electronics giving rise to the barrier. Second, experimentalists have not had a chance to explore "ideal" epitaxial, single-crystal, metal-semiconductor systems. This situation has changed with the recent development of silicide-silicon epitaxial growth techniques so that, for the first time, epitaxial, single-crystal, atomically abrupt, clean metal-semiconductor interfaces may be fabricated.[1] Consequently, a unique opportunity is now at hand to explore the physics of Schottky-barrier (SB) formation and electron transport across near perfect metal-semiconductor heterojunctions.

A system in which just such possibilites have been explored is the $NiSi_2$/Si heterojunction. $NiSi_2$ has been shown to grow epitaxially on the Si(111) surface in either one of two orientations termed *A* and *B*, in which the measured interface structure differs only in the positions of the third and higher nearest neighbors to the last nickel layer. Type-*A* $NiSi_2$ layers have the same orientation as the substrate, whereas type-*B* films share the normal $\langle 111 \rangle$ axis, but are rotated 180° with respect to the substrate.[2]

It was first reported by Tung that there is a significant difference in the measured Schottky-barrier height (SBH) between type-*A* and -*B* $NiSi_2$ layers grown on Si(111).[3] For *n*-type material, the SBH for type-*A* layers was measured to be 0.65 eV, against 0.79 eV for type *B*, the difference being $\Delta\Phi \sim 140$ meV. These results were later questioned by Liehr, Schmidt, Le Goues, and Ho, who claimed that both *A* and *B* layers could be produced with a high common barrier of ~ 0.8 eV on *n*-type silicon.[4] Subsequently, Hauenstein *et al.* published the results of their independent studies, concluding that their data supported the original findings of Tung.[5] In light of this apparent controversy, we have reexplored electron transport across $NiSi_2$/Si heterojunctions, and in a series of careful experiments in which *I*-*V*, *C*-*V*, and activation-energy determinations of SBH's were performed for both *n*- and *p*-type Si(111) substrates, the original conclusions of Tung's work were confirmed.[6]

In this paper, we describe a series of experiments in which we explored the possible role of bulk or interface defects in SBH formation in epitaxial $NiSi_2$/Si contacts. We show that the results of deep-level transient spectroscopy (DLTS) measurements, and *I*-*V* and *C*-*V* characterization following exposure to atomic hydrogen, are suggestive of an intrinsic mechanism for SBH formation. In addition, we demonstrate that under certain sample preparation conditions, there is an unintentional introduction of boron *p*-type impurities at the Si surface.

The samples were prepared by deposition and reaction of Ni on clean Si substrates under ultrahigh-vacuum (UHV) conditions. Details of the experimental procedures have been described elsewhere.[2] Electrically isolated diodes were delineated by etching mesas using standard photolithographic techniques. For room temperature *I*-*V* and *C*-*V* measurements electrical contact to the metal was made using a fine tungsten probe. For low-temperature measurements, including DLTS, the samples were bonded on TO-18 headers using an additional metallization layer.

DLTS was used to probe for the presence of deep-level defects beyond the zero-bias depletion region of the diodes (typically ~ 0.2–0.5 μm). The measurements were performed using a calibrated apparatus which combined a Boonton capacitance meter and a correlator.[7] In all samples investigated, i.e., *A*- and *B*-orientated layers grown on *n*-(arsenic doped) and *p*-type (boron doped) substrates, no DLTS signals could be detected. It should be pointed out that DLTS is not sensitive to "electrically inactive" defects (those which do not exchange charge with either the conduction or valence band of silicon), so we cannot, for example, rule out the possibility of metallic precipitates in the Si. Nickel precipitates, for which we have no direct experimental evidence, are possible because of the high diffusion coefficient $D \sim 2 \times 10^{-6}$ cm^2/sec and solubility $C_S \sim 10^{13}$ cm^{-3} of nickel at the growth temperature ($\sim 500\,^{\circ}$C) of the silicide. Given the sensitivity of our DLTS measurement system ($\sim 10^{-4}$ of the dopant concentration), our experimental results set an upper limit of 10^{11} cm^{-3} on the concentration of residual electrically active defects in the Si.

We have also explored the possibility that the measured

SBH's might be controlled by the presence of interface or near-surface defects (within the zero-bias depletion width) by exposing the diodes to atomic hydrogen. It is well known that hydrogen in silicon passivates shallow donors,[8] acceptors,[9] a large number of other point defects or impurities,[10] dangling bonds,[11] grain boundaries,[12] and even Si/SiO_2 interfaces.[13] Both bonded and unbonded samples were used to eliminate the possibility of contamination from the overlying metallization pads. Hydrogenation of the samples was achieved by exposing the samples to a 750-mtorr, 0.08-W-cm^{-2}, 30-kHz plasma for 3 h with the samples held at ~120 °C.

Evidence for the in-diffusion of H through the $NiSi_2/Si$ interface into boron-doped p-type Si(111) is shown by the free-carrier concentration profiles deduced from C-V measurements and illustrated in Fig. 1. As expected,[9] the electrical activity of the boron dopant is passivated, more than 1 μm below the interface. Typical results of forward-bias I-V measurements performed on these samples are displayed in Fig. 2. Beacuse of the low barrier heights on p-type material, these measurements were taken with the devices held at low temperature, using bonded samples. The measured SBH for A- and B-orientated samples is little affected by exposure to atomic hydrogen, and the difference, $\Delta\Phi$, in SBH's is unchanged. The small increase in SBH ~10 meV may, in part, be due to a decrease in the effective doping concentration. The initial electrical activity of the boron was recovered after annealing to 200 °C for 30 min. After this anneal, it was found that the measured SBH's returned to their initial values. Subsequent annealing at 300 °C resulted in no further change in SBH's.

In Fig. 3, we present typical forward-bias I-V characteristics measured before and after hydrogenation, for A- and B-orientated $NiSi_2$ on n-type Si(111). As may be seen, hydrogenation of type-A samples results in a small reduction in the measured SBH (~10 meV). The decrease in the measured SBH's of type-B samples is more pronounced. This, however, may be due to slight imperfections in the diodes as these particular samples had measured SBH's somewhat below the expected value of 0.79 eV.

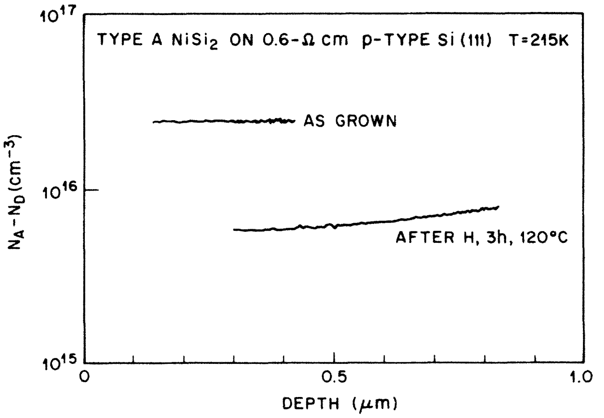

FIG. 1. Hydrogen passivation of boron deduced from C-V profiling before and after hydrogenation.

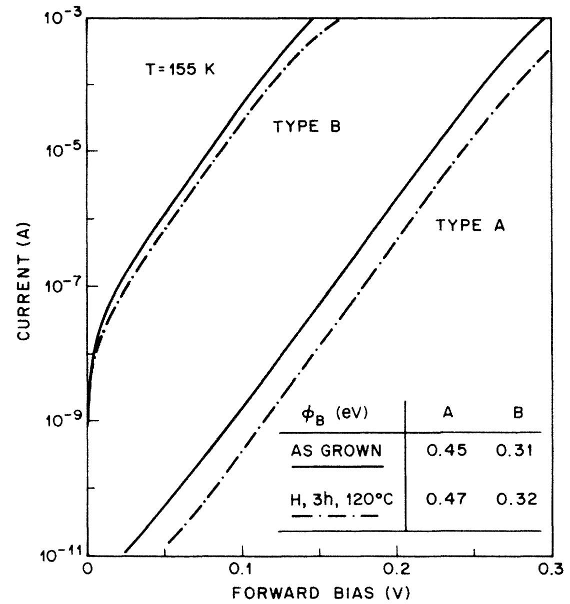

FIG. 2. Typical forward bias I-V characteristics before (solid curve) and after (dashed curve) hydrogenation of A- and B-orientated $NiSi_2$ on p-type Si(111).

Overall, our results show that the main SB formation mechanism for single-crystal-silicide interfaces is little affected by hydrogenation. These results suggest that defects, such as dangling bonds,[14] are not the cause of the difference in SBH's between A- and B-orientated $NiSi_2/Si$ interfaces. If such defects contributed to $\Delta\Phi$, then we would have expected a significant change in $\Delta\Phi$ after hy-

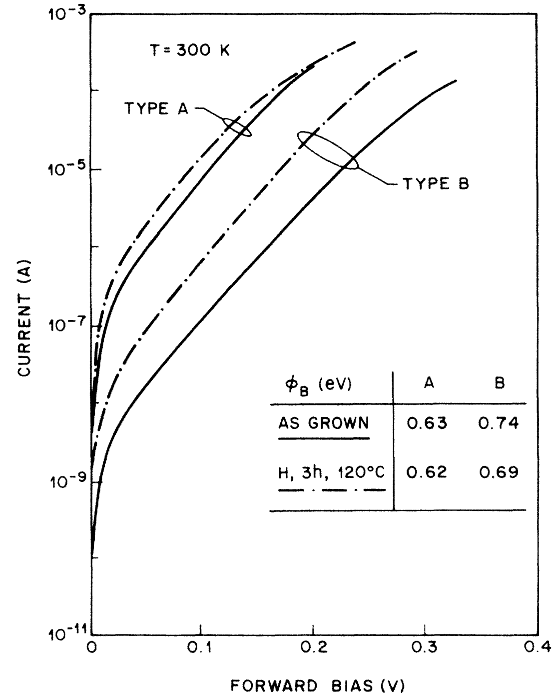

FIG. 3. Typical forward-bias I-V characteristics before (solid curve) and after (dashed curve) hydrogenation of A- and B-orientated $NiSi_2$ on n-type Si(111).

drogenation. A mechanism involving intrinsic interface states is consistent with these observations, and theories involving extrinsic defects are not directly supported by the present findings. However, because defects may exist which are not passivated by hydrogen and the passivation process may not be complete in our experiments, we cannot rule out extrinsic defects entirely. At present it is not clear whether the observed small effect of hydrogenation on SBH's is due to a change in the bulk electronic properties of the silicide.

In an attempt to elucidate the origin of the differences between the results of Tung[3] and Liehr *et al.*,[4] we have shown[6] that an acceptorlike defect or impurity is introduced in the surface region during a 10–120-sec high-temperature cleaning ($T_{\rm cl} \sim 1050\,^{\circ}{\rm C}$) under UHV. This gives rise to a high apparent SBH ~0.8 eV for type-*A* interfaces prepared on lightly doped *n*-type Si substrates ($n < 5\times10^{15}$ cm^{-3}). Low-temperature cleaning ($T_{\rm cl} \sim 850\,^{\circ}{\rm C}$) does not introduce a *p*-type impurity layer and the correct SBH is measured in these cases. Further evidence for the existence of this impurity layer is given in Figs. 4(a) and 4(b) which show free-carrier concentration profiles deduced from *C*-*V* measurements for NiSi$_2$/Si structures prepared on both *n*- and *p*-type substrates, respectively. The data clearly reveal the presence of a *p*-type contaminant with a maximum concentration of $\sim 1\times10^{16}$ cm^{-3}, which extends ~0.5 μm below the surface.

There exists considerable evidence in the literature that high-temperature cleaning *in vacuo* produces acceptor-type defects in silicon.[15-17] There is, however, no agreement on the microscopic nature of the defect. In an attempt to identify the impurities we have carried out complementary DLTS measurements on the *p*-type samples after high-temperature treatment and found no observable deep levels. Current transient spectroscopy revealed a single low-temperature feature associated with carrier freeze out on the shallow boron level. No evidence for aluminum or other *p*-type dopants was found. We tentatively conclude that the impurity diffusing from the surface during a high-temperature clean ($T_{\rm cl} \sim 1050\,^{\circ}{\rm C}$) is boron. This is consistent with the conclusions of some previous studies (e.g., Ref. 16). We note, however, that such identification does not seem to be compatible with the large penetration depth of the contaminant (relative to the known diffusion parameters of boron). In any event, our results show that spurious effects may be produced as a result of high-temperature cleaning in UHV, and therefore that such treatments should be avoided.

We have attempted to cancel the effect this surface *p*-*n* junction has on the apparent SBH's by hydrogenation. Because the *p*-type region should be partially compensated, it is likely that the surface will revert to *n*-type after hydrogenation. In this way SBH's which truly reflect the interface Fermi level position may then be measured. Preliminary results show that after hydrogenation, SBH's of samples with a surface *p*-*n* junction decrease to values similar to those observed for hydrogenated samples without the *p*-*n* junction.

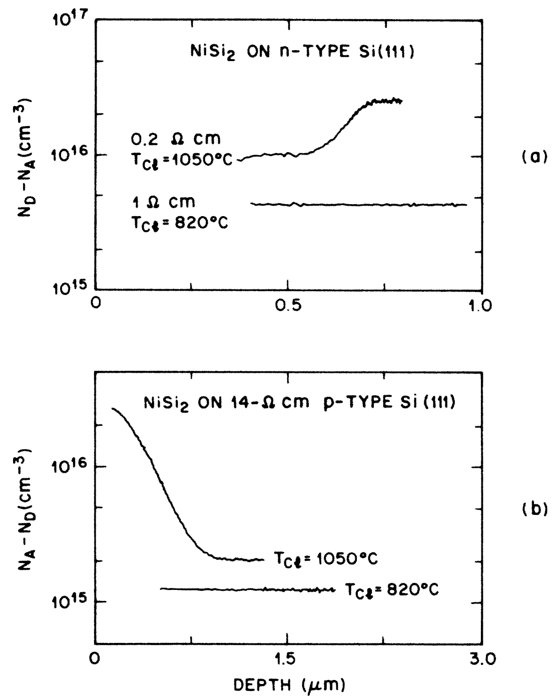

FIG. 4. Presence of *p*-type contaminant revealed by *C*-*V* profiling for (a) *n*-type and (b) *p*-type substrates after a high-temperature clean ($T_{\rm cl} \sim 1050\,^{\circ}{\rm C}$ for 120 sec). For $T_{\rm cl} \sim 850\,^{\circ}{\rm C}$ no contamination is detected.

In summary, we have carried out a series of experiments to explore the possible role of bulk and interface or near-surface defects in determining SBH's in epitaxial NiSi$_2$/Si heterojunctions. The results are consistent with an intrinsic mechanism for the difference in SBH's measured for type-*A* and -*B* interfaces. In this paper we have tentatively identified boron as the *p*-type surface contaminant occurring as a result of high-temperature cleaning. In addition we suggest that all SBH measurements which used high-temperature cleaning procedures during diode fabrication[4] be interpreted with caution.

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