Electronic States at Silicide-Silicon Interfaces

Paul S. Ho
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

and

Edward S. Yang, Howard L. Evans, and Xu Wu
Department of Electrical Engineering, Columbia University, New York, New York 10027

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A capacitance-spectroscopy technique based on accurate phase detection has been developed to measure the unoccupied states at silicide-silicon contacts. For Pd and Ni silicides, a dispersed group of states was found to exist in the Si band gap with its peak at a level 0.63–0.65 eV above the valence-band edge. Silicide formation alters their density and distribution to reflect the changes in the structural perfection and barrier height. Observations on the epitaxial $NiSi_2$-Si(111) interfaces reveal that the characteristics of these states are controlled by the degree of structural perfection of the interface instead of the specific epitaxy. This seems to be the first correlation of the structural and electronic properties of a silicide-silicon interface.

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Ever since Bardeen proposed the surface-state model[1] as the basis of Fermi-level pinning at metal-semiconductor interfaces, the existence and nature of interface states have become the central issues for the understanding of Schottky-barrier (SB) formation. Many early studies have focused on systems with weak metal-semiconductor interaction where the existence of interface states in the band gap has often been attributed to metal penetration into the semiconductor.[2] In the past several years, with the development of microanalytical techniques, it has been found that the interaction at a metal-semiconductor interface is generally not weak and reactions frequently occur, resulting in atomistic changes of the layer, e.g., compound formation, defect generation, and interatomic mixing.[3-6] These phenomena modify the stoichiometry, atomic environment, and microstructure of the interface, which can change the basic nature of the interface states.

These effects are important for understanding Schottky-barrier formation at the silicide-silicon interface where the silicide compound is formed by reaction between the transition metal and silicon atoms. It is known that silicide formation dominates the interfacial chemistry and the interface is structurally abrupt but contains defects such as atomic steps and misfit dislocations.[3] The Schottky barrier was found to be a true interface property and its nature can be classified as extrinsic or intrinsic, depending on the extent of the reaction.[7] In spite of the progress, the central issue regarding the nature of the interface states at the silicide-silicon interface remains unresolved. The difficulty lies in the fact that the analytical techniques used so far are primarily surface electron spectroscopies which do not have the required sensitivity and energy resolution (< 0.1 eV) to detect the presence of interface states of an amount (about 10^{13} states/cm^2) sufficient to pin the Fermi level (E_F). This is illustrated by the Auger study of the Pd_2Si-Si interface[8] where interface valence states of Si were observed and their position appears to be below E_F. However, the intensity and distribution of these states cannot be accurately measured to assess their role in determining the electrical properties of the interface.

In this regard, particularly interesting are the recent results of the $NiSi_2$-Si(111) interface, where a difference of 0.14 eV in barrier height has been reported for the twin epitaxial (A and B type) interfaces.[9] A later study found, however, that these two interfaces have similar barrier heights although both exceed the mixed type by about 0.14 eV.[10] These are the first observations on the correlation of structure to barrier height, which, if clarified, is of basic importance for understanding SB formation. So far there are no other electrical measurements available to resolve the discrepancy.

To measure the interface states, electrical techniques designed specifically for metal-semiconductor contacts are required. For this purpose, we have developed a capacitance-spectroscopy technique[11] and have used it to study a number of silicide-silicon interfaces. In this Letter, we present the results of Pd and Ni silicide-silicon interfaces. The Pd results reveal for the first time the characteristics of the states at the silicide-silicon interface as well as the effects due to interfacial reactions. The Ni results were obtained from the single A and B and mixed AB types of the $NiSi_2$-Si(111) epitaxial interface. The observed interface states reveal that the characteristics for the two single-type interfaces are similar but more perfect than the mixed-type interface. This establishes a direct correlation of the interface state characteristic to the structural perfection. The Ni results can clarify the discrepancy on the barrier-height measurements by suggesting that the barrier height is controlled by the structural perfection instead of the specific epitaxy of the interface.

One basic difficulty in measuring interface states at a metal-semiconductor contact arises from the localized nature of the interface states, as close as a few angstroms from the metal. This invalidates the use of standard techniques, e.g., reverse-biased capacitance and deep-level transient spectroscopy. The problem is solved in our study by measurement of the induced capacitance of the contact under a foward-biased voltage with use of a phase-sensitive spectroscopy technique. A dc voltage is applied to fill the interface states below the quasi Fermi level E_F while a small ac voltage is used to probe the presence of the filled states by measuring the capacitance that they induce. The nature of the interface states can be deduced from the magnitude of the induced capacitance and its frequency dependence. One general problem in this kind of measurements arises from the conductance (in-phase) component in the Schottky contact under the forward-biased condition. Its magnitude can be several orders higher than the capacitance (out-of-phase) component; therefore, it is essential to maintain a precise zero-phase condition during the measurement. The details of the measurement can be found elsewhere.[11]

In our experiment, *n*-type (111) silicon samples were chemically or UHV cleaned before metal evaporation, and an aluminum back contact was provided. The UHV cleaning was carried out by several heating steps and a flash to 1100 °C for a few seconds. The barrier height was measured with *I-V* (*in situ*) and photoresponse techniques. The interface state measurement was made outside the vacuum system by carrying out capacitance-versus-voltage scans as a function of temperature and frequency (from 20 Hz to 3 kHz).

In Fig. 1, the capacitance curves obtained at 100 Hz and room temperature for a chemically cleaned Ps_2Si/Si diode show a distinct peak at 0.28 eV for the as-deposited interface. Measurements at other frequencies showed that the amplitude of the capacitance component decreases with increasing frequency, and becomes negligible at about 1 KHz. The low-frequency response demonstrates a long time constant associated with these interface states. The data obtained at other frequencies and temperatures indicate that a charge-capturing model based on a single time constant is inadequate to describe the diode behavior. While studies are in progress to evaluate the density and distribution of the interface states from the temperature and frequency data, we can estimate the number of charge states from the integrated capacitance at low frequency.[12] If a simple model which takes into account charge exchange solely with the conduction band is used, then the peak position specifies the location of the states relative to the Fermi level while the peak area represents the density of states. On this basis and using a measured barrier of 0.75 eV for this diode, we deduce a peak for the unoccupied states at 0.62 eV above the valence-band edge and the data at 20 Hz correspond to a total density of states of about $10^{13}/cm^2$.

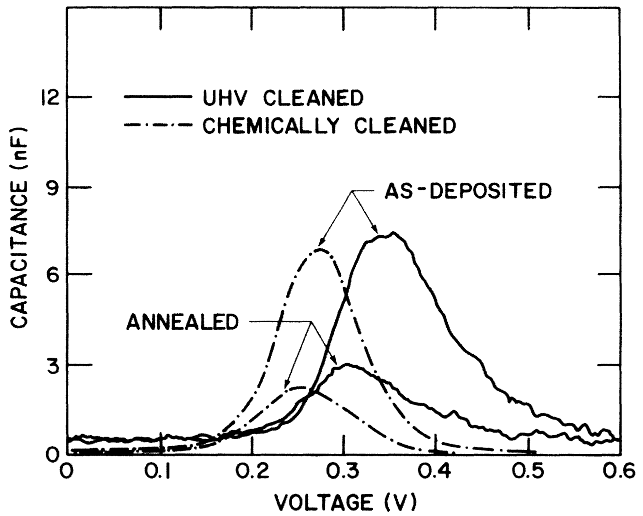

FIG. 1. Effect of annealing on the capacitance spectra observed for UHV cleaned and chemically cleaned Pd-Si(111) interfaces. All measurements were made at 100 Hz.

The effect of silicide formation on the nature of the interface states for this contact can be observed from its annealing behavior. The annealing condition, 250 °C for 30 min, was chosen to convert the as-deposited interface into a well-reacted Pd_2Si/Si interface. As shown in Fig. 1, the total density of states after annealing decreases by a factor of about 3 while its distribution is sharpened. In addition, the spectral peak shifts down by 30 mV, which corresponds to the change observed in the barrier height.

The behavior of the states observed for an UHV interface before and after annealing (Fig. 1) is similar to the chemically cleaned interface, except that the peak for the as-deposited UHV interface is shifted upward for about 50 meV, corresponding to a higher barrier height of 0.79 eV. Comparable reduction in the total density (4×) and downward shift of peak position (45 mV) were observed after annealing and the latter correlates to the decrease to 0.73 eV in the barrier height. On the basis of the measured barrier height, the peak of the unoccupied states at the reacted interface is about 0.64 eV above the valence-band edge. The observed behavior demonstrates the true interface nature of these states. For the as-deposited case, the interface contains extrinsic interface defects, e.g., oxide and contaminants, which give a high density and broad distribution of these states. As the reaction proceeds to establish a more perfect interface, the density of interface states is reduced substantially while its distribution becomes sharpened. It is significant that the distributions of the unoccupied states for the two annealed interfaces are quite similar, showing that silicide formation changes two different initial interfaces (chemically cleaned or UHV prepared) to one with similar characteristic states. This demonstrates that silicide formation, if properly controlled, can yield an interface with reproducible and more perfect characteristics regardless of the condition of the initial metal-silicon interface. Electronic states with similar peak position (at 0.30 eV above the Fermi level) have been detected previously by electron energy-loss spectroscopy at the Pd-n-Si interface.[13]

More striking correlation of the structural perfection and interface states was observed at the epitaxial Ni silicide interfaces. As shown in Fig. 2, similar densities and peak positions of the interface states were observed for the two single types, which are distinctly different from the mixed type. Again the peak positions correlate well with the difference in barrier heights. The type A and B spectra both peak at 0.34 V, signifying a band of states around 0.65 eV from the valence band. Contrasted to this, the type AB mixed interface has a much broader spectrum, peaking at 0.21 V. When we take into account the lower barrier height of this interface, the state is 0.64 eV from the valence band, the same as the single-phase interfaces. The single-type interfaces have a low density of states, about $10^{12}/\mathrm{cm}^2$. This is about a factor of 5 to 10 times less than the mixed interface. Significantly, the type-A interface has about twice as many interface states as the type-B interface although their peak positions are identical. It is known that the type-A interface is thermally less stable and hence more difficult to form, so that the higher interface state density reflects the presence of more defects at this interface.

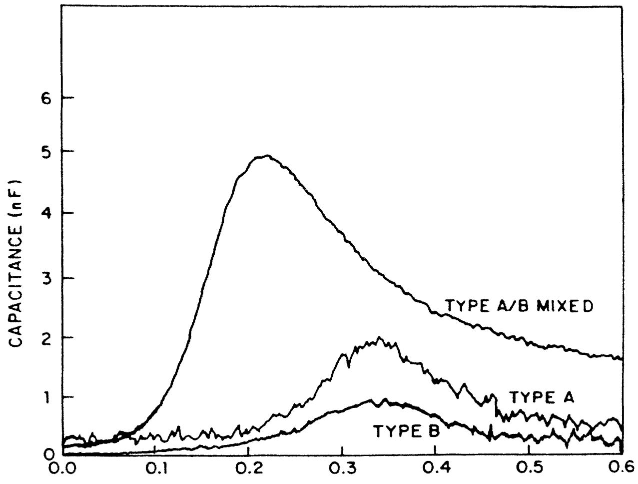

FIG. 2. Capacitance spectra observed at 100 Hz for three epitaxial $NiSi_2$-Si(111) interfaces: the A and B single-phase types and a mixed AB type.

Our results can be represented by the schematic band diagram based on the simple charge-exchange model (Fig. 3). Even though a model including other exchange mechanisms is used, the distribution can be vastly different, possibly leading to a more dispersed band distribution. This uncertainty will not change our qualitative conclusion that the characteristics of the interface states are very similar for the single-type and mixed-type silicides except for the difference in the densities, which shows that the single-type interfaces are more perfect. The almost identical peak positions indicate that these states are likely associated with the same kind of imperfections, most probably bonding defects of the silicon atoms at, or very close to, the interface. This suggests that the different barrier heights of these interfaces are determined by the amount of defect states available to pin the Fermi level which, in turn, is controlled by the degree of structural perfection of the interface, rather than by the specific epitaxy.

We have studied a number of silicide-Si interfaces and found interface states with distributions and characteristics close to those reported here. In general, similar effects of annealing on the distribution and density of the states were observed and the direction and amount of the shift correlate with the change in the barrier height. This seems to be the general trend of the effect of silicide formation on the electrical characteristics of the interface.

In summary, we have observed a dispersed group of unoccupied states existing in the Si band gap at the silicide-Si interface. Upon annealing, their density and distribution change to reflect a more perfect interface as a result of silicide formation. The observation on

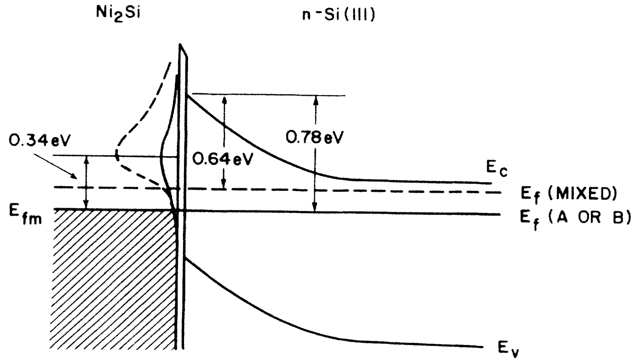

FIG. 3. Schematic diagram for the distribution of the unoccupied states at $NiSi_2$-Si(111) interfaces. The solid curve represents the single-phase interface and the dashed curve represents the mixed-phase interface. Note the different positions of the Fermi level corresponding to the difference in the barrier heights observed.

the Ni silicides shows that their character is influenced strongly by the degree of perfection of the interface. The nature of such defects remains to be clarified. Although structural defects specific to the interface have been observed by high-resolution transmission electron microscopy for several silicide-silicon systems, including the $Pd_2Si/Si(111)$ interface,[14] it is not clear whether such defects can account for the observed states. Recently Si dangling bonds of interfacial vacancies have been proposed to account for Fermi-level pinning in silicide-silicon interfaces.[15] It would be very interesting to check whether our results which reveal the empty instead of the occupied states are consistent with this particular model.

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