Correlation of Schottky-Barrier Height and Microstructure in the Epitaxial Ni Silicide on Si(111)

M. Liehr,[a] P. E. Schmid,[b] F. K. LeGoues, and P. S. Ho
IBM T. J. Watson Research Center, Yorktown Heights, New York 10598
(Received 13 February 1985)

The correlation of Schottky-barrier height and microstructure has been investigated with three types of epitaxial Ni silicides, type-*A* and -*B* $NiSi_2$ and NiSi, on Si(111) substrates. All these interfaces can be formed to yield a barrier height of 0.78 eV. This high barrier was obtained only for near-perfect interfaces; otherwise-less-perfect silicides yielded low barrier heights of 0.66 eV. This barrier height is controlled primarily by the structural perfection of the interface rather than by the specific type of epitaxy.

PACS numbers: 73.30.+y, 64.80.Gd, 68.48.+f

In the past several years, there has been extensive interest in the study of the formation of the Schottky barrier at the silicide-silicon interface. This class of interfaces can be formed to have specific stoichiometry and structure by contol of the reaction kinetics of silicide formation. This makes it well suited for investigation of the basic question of the correlation between the electrical barrier properties and the material characteristics. Several studies have been carried out with Ni and Pd silicide, taking advantage of the wide variety of interfaces formed in these systems.[1-3] Results of these studies showed that materials characteristics, such as the stoichiometry, microstructure, and substrate orientation, do not affect the barrier height; only the defects incorporated at the interface have a measurable effect on the barrier height. This led to the classification of the interface as intrinsic and extrinsic based on the amount of defects remaining at the interface after silicide formation.[4]

Recently, barrier heights of 0.14-eV difference have been reported for type-*A* and type-*B* epitaxial-$NiSi_2$ on Si(111) interfaces.[5] This study has generated great interest since this is the first demonstration of the effect of the interfacial microstructure on the barrier height, which, if confirmed, is of basic importance to the understanding of Schottky-barrier formation. It was suggested that the barrier height of the type-*B* interface is determined by a mechanism different from type *A*, most likely intrinsic electronic states.[5,6] On this basis, one can explain the previous results which were measured on mixed *AB* interfaces as determined by whatever mechanism is responsible for the type-*A* interface. It is most intriguing, however, why the barrier height of such similar epitaxial interfaces would be determined by distinct mechanisms. (Types *A* and *B* are related by a 180° rotation with respect to the normal of the Si substrate and their interfacial atomic configurations differ only in the third and fourth neighbors.)

To investigate this question, we have carried out a series of measurements on the epitaxial-Ni–silicide interfaces, including the type-*A*, type-*B*, and the mixed *AB* interfaces. Results of our measurements showed that both types of interfaces have the same average barrier height of 0.78 ± 0.02 eV, in contrast to Tung's measurements where type *A* exhibited a low barrier of 0.65 eV. The result that specific structure is not a prime factor in determination of the barrier height was further supported by a similar barrier height, 0.78 eV, found for a third epitaxial interface of the NiSi phase (type *C*). In addition, it was observed that the high barrier height was obtained only for almost-perfect epitaxial silicides: Otherwise-less-perfect silicides even of single types, as prepared by a different annealing method or by incorporation of carbon and oxygen impurities, yielded low barrier heights of 0.66 eV. Our results suggest that the variation of the barrier height depends primarily on the structural perfection of the epitaxial interface since it determines the nature and density of the interfacial defects, but the type of epitaxy is not important.

Experiments were carried out in an UHV chamber (base pressure 10^{-8} Pa) which was equipped with uv photoemission and Auger-electron spectroscopy and facilities for *in situ* electrical measurements. Samples were prepared from *n*-type Si(111) wafers (phosphorous doped and 8–12 Ω cm) and an Ohmic Ta back contact was provided for electrical measurements. Before metal evaporation, the sample surface was cleaned by several heating steps including a flash to 100 °C for several seconds. Ni was *e*-beam evaporated from a separately pumped chamber in order to avoid contaminations. The Si surface and the Ni film prepared by this procedure showed no trace of C and O as detected by uv photoemission and Auger-electron spectroscopy. Sample temperatures were measured with a calibrated infrared pyrometer and the accuracy of absolute temperature determination was estimated to be ±25 °C.

The epitaxial interfaces were prepared by first forming template structures.[7] For type-*A* and type-*B* interfaces, the template structures were formed by depositing 17 to 20 Å and less than 6 Å, respectively, and then annealing in a temperature range of 450 to 500 °C

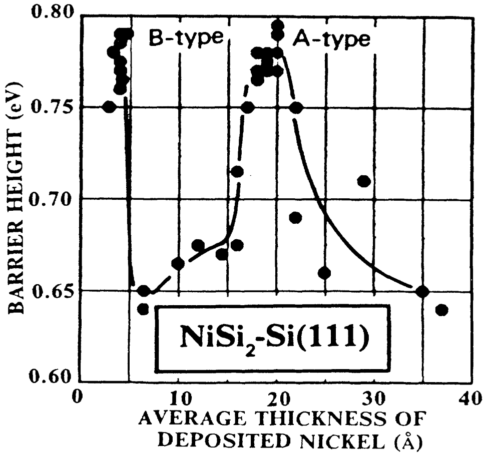

FIG. 1. Schottky-barrier height of $NiSi_2$ films on Si(111) prepared for different average initial Ni layer thicknesses followed by a heat treatment to 450 °C (template method). Repeated deposition-annealing cycles yielded a silicide layer thickness between 60 and 120 Å. Single-phase type A and type B form for initial Ni thickness of 17–20 Å, respectively.

for 3 to 5 min. The type-C interface was formed by a similar procedure with a template Ni thickness of 1.3 to 2 Å and 250 °C annealing.[8] The silicide phase and microstructure of the interface before and after reaction were identified by transmission electron microscopy (TEM) and ion backscattering techniques. The type-C interface was found to be that of NiSi. The silicide thickness used for barrier height measurements was always above 60 Å in order to avoid complications due to incomplete coverages. Such layers were obtained by repetition of the initial deposition-annealing sequence until the desired thickness (between 60 and 120 Å) was reached.

In each run, Ni was evaporated through a metal mask defining three rows of diodes of 0.6, 1.3, and 2.5 mm in diameter and a blanket area. This was designed so that electrical measurement and structural analysis could be carried out on the same sample. Diode characteristics were measured by current-voltage (I-V) and photoresponse measurements. The former was performed *in situ* with Au wires as contacts while the latter was made outside the vacuum system. The values obtained from these two measurements usually coincided within ± 0.02 eV; I-V measurement repeated in air after initial *in situ* measurement yielded virtually the same barrier height.

Barrier heights of the epitaxial interfaces have been measured as a function of the Ni template thickness and the results are summarized in Fig. 1. Not shown here is the value of the ideality index in the I-V characteristics. Its value was found to fall in the range from 1.00 to 1.30 with only very few exceeding 1.15 and depended somewhat on the substrate alignment; it clustered in the range of 1.05 to 1.3 for 1°–2° misalignment and in the range of 1.00 to 1.03 for 0.25° misalignment. The substrate alignment was found to have no effect on the barrier height.

The structures of type-A and type-B interfaces have been verified by cross-sectional TEM using several samples for each type. Both interfaces exhibited atomically flat structures, as shown in Figs. 2(a) and 2(b). Samples with a mixed orientation showed a less flat interface where boundaries separating different phases and orientations were clearly observable [Fig. 2(c)]. The size of the phase domains was in the order of

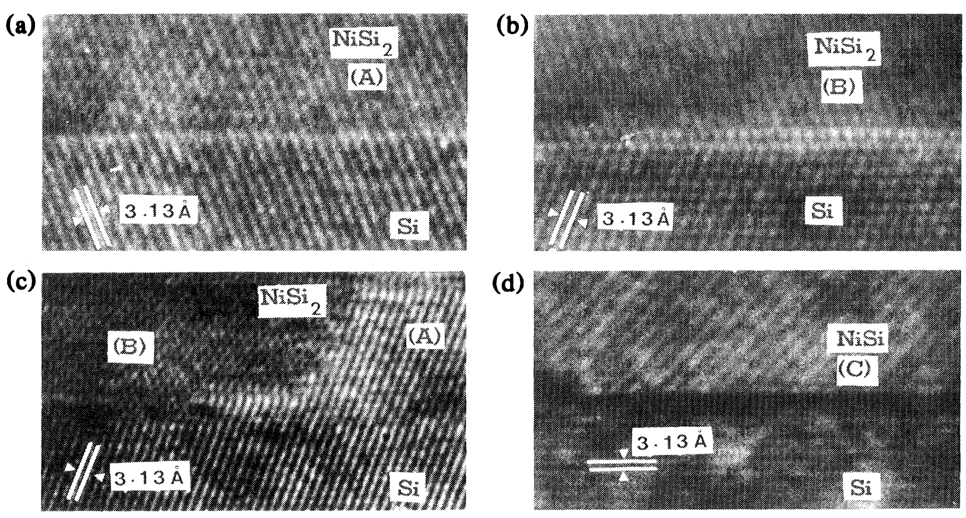

FIG. 2. Cross-sectional TEM pictures of samples with a 60-Å-thick silicide film on Si(111). The samples shown are (a) pure type A, (b) pure type B, (c) AB mixed $NiSi_2$, and (d) pure type-C NiSi.

10–100 nm.

Results in Fig. 1 clearly show that pure type-A and type-B interfaces have the same barrier height which is higher than for the mixed phase. This differs from the previous results of Tung who found a barrier height of 0.65 eV for the type-A interfaces. Our finding is further supported by the results obtained for the type-C interface, as shown in Fig. 3. The microstructure of this interface is shown in Fig. 2(d). One can see that this interface has a different silicide, a $NiSi$, but it can be formed to yield the same barrier height as the A and B interfaces.

During the course of this study, one interesting result seemed to emerge. This was the observation that the high barrier height can be obtained only with careful control of the formation condition of the silicide. Rather small deviations from the proper range of the template thickness and annealing temperature would result in lower barrier heights. This was particularly sensitive in the case of the type-C interface, as evidenced from Fig. 3 where the majority of the samples were not perfect enough to achieve a higher barrier height. Similar results can also be observed, although to a lesser extent, in Fig. 1 for the A and B interfaces. Cross-sectional TEM revealed these interfaces to be less perfect, containing phase-domain boundaries with faceted or stepped structures.

This suggested that the degree of perfection of the interfacial structure may be important in determination of the barrier height. Two sets of experiments were carried out to test this hypothesis, one as a function of annealing temperature and the other by incorporating impurities at the interface. The temperature experiments have been carried out in the range of 250 to 600 °C for A and B interfaces. The barrier heights were found to be consistently high between 450 and 500 °C and TEM observations of such samples showed the most perfect, atomically flat interfaces. Above 500 °C the silicide film started to aggregate, the interfacial structure deteriorated, and the barrier height started to decrease when a certain density of islands was exceeded. This was particularly clear for the type-A interface which is known to be more difficult to form than type B. It is interesting that an A sample that was reacted to only 400°C already showed a high barrier height of 0.75 eV but TEM revealed its interface to contain a mixture of very large grains (>100 nm) of A, B, and even less-reacted $NiSi$ structure. This observation indicates that a certain threshold in the density of grain boundaries or associated defects has to be reached at the interface in order to obtain a low barrier height. Cross-sectional TEM is unfortunately not a good technique to investigate density of defects, first because statistics are bad and secondly because it cannot give information on density and type of point defects present at the interface. It is only possible to give an order of magnitude estimate, namely, that, when the grain size is more than about 100 nm, the barrier will remain high, and when the grain size is less than this value, the barrier will be low.

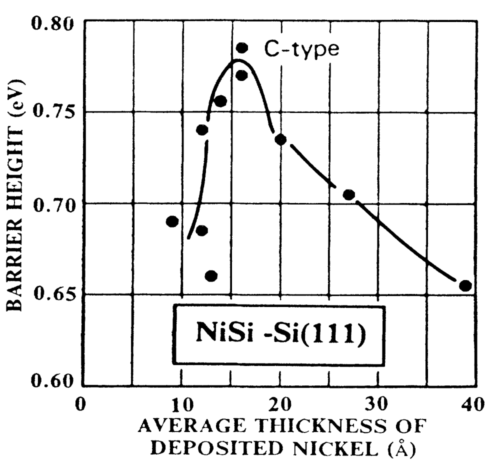

FIG. 3. Schottky-barrier height of $NiSi$ on Si(111) for samples prepared for different average initial Ni layer thicknesses between 0.8 and 4 Å followed by a heat treatment to 250 °C, and repeated deposition-annealing cycles up to layer thicknesses of more than 60-Å $NiSi$. Pure epitaxial $NiSi$ forms between 1.3- and 2-Å initial Ni coverage.

The impurity experiments were carried out by the incorporation of a controlled amount of carbon and oxygen impurities at the single-phase A and B interfaces. TEM showed that under carbon incorporation the single-phase structure was retained at the interface but that the interface was very heavily stepped and the barrier height was reduced to about 0.66 eV, similar to the mixed interface. Oxygen impurities, especially at higher concentrations, were found to render the single-phase layers first mixed AB and finally polycrystalline, and thereby decreased the barrier height. The strong dependence of Shottky-barrier height on defects induced by sample preparation might be responsible for the difference in the Shottky-barrier height found by Tung for the more difficult to form type-A interfaces. It is also possible that the barrier height may be a function of initial Si cleaning steps and/or doping.

A related study was carried out to clarify further the nature of the high- and low-barrier interfaces by measurement of the density of the interface states. This was based on a capacitance spectroscopy technique which is capable of detecting the density and distribution of the unoccupied states above the Fermi level. While details of this study will be published elsewhere,[9] it suffices to mention that the results of such measurements indicated important differences in the interface state characteristics for these interfaces. The single-phase high-barrier interfaces were found to have a low density of states of only about 10^{12} to $10^{13}/cm^2$, which is about an order of magnitude less than that of the low-barrier interfaces. In addition, they were located at different energy positions in the band gap. While the implication of these results on the barrier height have yet to be understood, it seems clear that the degree of perfection of the interface strongly influences the nature of the interface states.

In summary of all these results, our studies show that the epitaxial-Ni–silicide interface can be properly prepared to yield a high Skottky-barrier height 0.78 eV. Imperfections of only a minute amount, being incorporated during interface formation as a result of silicide growth or by absorption of impurities, can lower the barrier height to 0.66 eV. The barrier height seems to be determined more by the degree of perfection of the interface than by the type of compound structure at the interface.

This work was supported in part by the U. S. Office of Naval Research.

[a]Permanent address: Laboratoire ESCA, Institut de Recherche sur les Interfaces Solides, Facultés Universitaires Notre Dame de la Paix, Namur, Belgium.

[b]Permanent address: Ecole Polytechnique de Lausanne, Lausanne, Switzerland.

[1]M. Iwami, K. Okumo, S. Kamei, T. Ito, and A. Hiraki, J. Electrochem. Soc. **80–82**, 102 (1980).

[2]G. Ottaviani, K. N. Tu, and J. W. Mayer, Phys. Rev. B **24**, 3354 (1981).

[3]P. E. Schmid, P. S. Ho, H. Föll, and T. Y. Tan, Phys. Rev. B **28**, 4593 (1983).

[4]P. S. Ho, J. Vac. Sci. Technol. A **1**, 745 (1983).

[5]R. T. Tung, Phys. Rev. Lett. **52**, 461 (1984).

[6]J. Tersoff, Phys. Rev. Lett. **52**, 465 (1984).

[7]R. T. Tung, J. M. Gibson, and J. M. Poate, Phys. Rev. Lett. **50**, 429 (1983).

[8]J. Clabes, M. Liehr, F. K. LeGoues, and M. Wittmer, to be published.

[9]E. S. Yang, H. Evans, M. Liehr, and P. S. Ho, to be published.

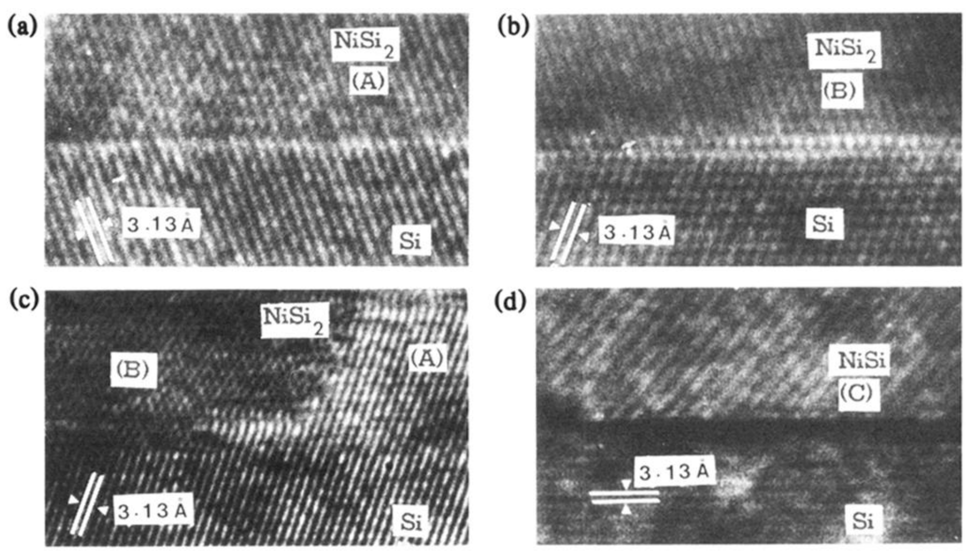

FIG. 2. Cross-sectional TEM pictures of samples with a 60-Å-thick silicide film on Si(111). The samples shown are (a) pure type *A*, (b) pure type *B*, (c) *AB* mixed $NiSi_2$, and (d) pure type-*C* NiSi.