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# Influence of thin $SiO_2$ interlayers on chemical reaction and microstructure at the Ni/Si(111) interface

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Surface electron spectroscopies (Auger electron spectroscopy and ultraviolet photoemission spectroscopy) and electron microscopy (scanning and transmission) have been used to study the influence of interfacial $SiO_2$ on the reactivity of the Ni/Si(111) interface. Iterated Ni depositions (up to ~75 Å thick), at room temperature, on Si oxide layers of various thicknesses [grown on Si(111)] were made in ultrahigh vacuum and followed by *in situ* annealing up to 900 °C. It was found that Ni initially agglomerates into islands at room temperature and above. Furthermore, at elevated temperatures the Ni reacts with the underlying Si through pinholes in the oxide to form $NiSi_2$. A higher temperature was required to initiate the silicide formation reaction for thicker $SiO_2$ layers, suggesting that the reaction is limited by mass transport through pinholes in the oxide. Direct Ni-$SiO_2$ interaction, in contrast, is rather limited. Some $SiO_2$ decomposition may take place at elevated temperatures and at such favorable sites as pinholes and structural defects in the oxide or areas adjacent to silicides. The low Schottky-barrier height found for reacted contacts (0.60±0.04 eV) was comparable to that obtained at nonperfect, oxide-free Ni silicide/*n*-type Si(111) interfaces.

## INTRODUCTION

The study of the silicon—transition-metal interfaces has been considerably expanded in recent years. The motivation for such studies comes from the aim of understanding the microstructure and chemical and electronic properties which determine the electrical characteristics of these technologically important contacts. Considerable progress has been made by carrying out experiments under well-controlled conditions and applying techniques which provide detailed chemical or structural information about the interface.[1,2] In order to develop a general understanding of Si Schottky-barrier properties, it is necessary to establish a relationship between the electrical characteristics of the contact and the microscopic chemistry and structure of the interface. The Ni/Si system has recently attracted special interest since it is one of the few systems known to form near-perfect epitaxial interfaces.[3] Furthermore, we have found that the electrical characteristics depend on the quality of epitaxy of the interface.[4] Further progress in the understanding of Schottky-barrier formation can be expected to come from a careful study of the Ni-Si interaction and a study of the influence of well-characterized impurities on this interaction and on the barrier formation.

The intention of this paper is to determine the effect of a silicon-oxide interlayer on the silicide formation and on the microstructural and electrical characteristics of the interface. Ultraviolet photoemission spectroscopy (UPS) and Auger electron spectroscopy (AES) were used to monitor chemical reactions at the interface; the microstructure was characterized by high-resolution transmission electron microscopy (TEM) and scanning electron microscopy (SEM) and the Schottky-barrier height values were derived from electric measurements.

## EXPERIMENTAL

Experiments were carried out in a three-chamber ultrahigh-vacuum (UHV) system (operating pressure, $10^{-10}$ Torr). The main chamber was equipped with UPS and AES and a facility for *in situ* electrical measurements. An evaporation chamber, connected to the main chamber via a conductance limiting tube, allowed metal depositions onto the sample in the main chamber with the pressure at the sample in the low $10^{-10}$ Torr range. Finally, an introduction and/or preparation chamber afforded rapid sample exchange, annealing to $\geq 1200$ °C, and UHV gas exposures up to 1 atm (e.g., for *in situ* oxidation).

The samples were cut out from Si(111) wafers (*n*-type, phosphorus-doped, 8—12 Ω cm). *In situ* electrical measurements as well as high-temperature anneals were possible by converting the back side of the samples into high-temperature ohmic contacts; these were fabricated by $n^+$-ion implantation at 300 keV followed by deposition of an ~1000-Å-thick layer of Ta. A gold-tipped electrode, placed in contact with the specimen surface (before and/or after metallization) by means of a mechanical feedthrough, allowed *in situ* electrical measurements. *In situ* sample annealing was performed by direct resistive heating. The samples were cleaned before introduction into the system by alcohol rinsing followed by drying in a nitrogen stream; inside the UHV system they were further cleaned by *in situ* annealing to 900 °C for a few minutes, followed by a brief flash to 1050—1100 °C for a few seconds. The pressure never exceeded $2\times10^{-9}$ Torr during the course of this treatment. As assessed by AES, UPS, and SEM, this specimen processing was found to produce clean Si surfaces, free of detectable defects. The sensitivity of the Auger equipment used was estimated to be $2\times10^{-3}$ for the detection of carbon on a silicon surface (C *KLL* to Si *LVV* line-intensity ratio). Sample temperatures during annealing and oxidation were measured with an ir-pyrometer that had been calibrated against a Chromel-Alumel thermocouple. The accuracy of the absolute temperature determination is estimated to be ±25 °C.

*In situ* UHV dry thermal oxidation at 100 °C and 80–160 Torr $O_2$ for about one minute produced oxide layers exhibiting UPS and Auger spectra typical of high-temperature-grown device-quality $SiO_2$. These thin (5–50 Å) oxide interlayers studied here are therefore being referred to as $SiO_2$. No impurities could be detected with AES in these oxides and the UPS spectra revealed a very low density of states in the gap. Qualitative analysis by SEM indicated that the surface roughness of the oxide films depends strongly on both temperature and oxygen partial pressure during oxidation, being smoother at higher oxygen pressures and temperatures. Longer oxidation times yielded larger oxide thicknesses and consequent charging effects in the photoemission spectra (for oxide thickness $>50$ Å). The oxide thicknesses were estimated using the escape depth of the Si *LVV* Auger electrons and checked by TEM after removal from the vacuum system.

Nickel was evaporated with an electron-beam evaporator over a distance of 55 cm. The sample remained at room temperature during deposition. Deposition rates varied up to a maximum of 0.02 Å/sec. The pressure in the evaporation chamber always remained in the low $10^{-10}$-Torr range, i.e., essentially at the base pressure of the main chamber. Under these conditions the deposited metal films were impurity free within the detection limit of AES. The Ni layer thickness was determined by a quartz crystal oscillator calibrated by Rutherford backscattering spectrometry (RBS) and checked by cross-sectional high-resolution TEM.

Heat treatments were performed by resistive heating under UHV conditions. The duration of each heat treatment was one minute. *In situ* current-voltage measurements were performed to determine Schottky-barrier characteristics as a function of processing. After removing the sample from the vacuum system, photoresponse measurements were performed to further assess the Schottky-barrier height and the overlayer structure and/or morphology was checked by SEM. Compound formation and microstructure of reacted and as-deposited films were determined by cross-sectional and flat-on TEM, using a Phillips 400ST microscope.

## ROOM-TEMPERATURE DEPOSITION

Integrated Auger electron spectra in the vicinity of Si *LVV* are shown in Fig. 1, for iterated coverages of Ni, deposited at room temperature, onto $SiO_2$-covered Si(111) samples. The average Ni overlayer thicknesses studied ranged from 0.8 to 50 Å, and the $SiO_2$ layers used were either thick ($\sim 30$ Å) or thin ($\sim 5$ Å). The lowest spectra in the figure are of the substrates before the Ni evaporation. The thick and thin $SiO_2$ substrates can be clearly distinguished by the Si *LVV* transitions shown. As is well known, this transition line is markedly affected by oxidation. It shifts from 89 eV for clean Si to 75.5 eV for $SiO_2$ (Ref. 5) [in integrated, $EN(E)$ versus $E$ spectra] and splits into two main satellites (at 75.5 and 62 eV), as is shown in Fig. 1 for both types of oxide used. The intensities of both the Si *LVV* and the O *KLL* lines of the $SiO_2$ decrease rapidly with increasing Ni coverage, the former with a typical attenuation length of 7–10 Å, the latter with a length of 15–20 Å. These values are in reasonable agreement with electron escape depth values at the corresponding kinetic energies.[6] One can therefore assume that for thickness $\geq 5$ Å the deposited Ni layer is essentially unreacted and homogeneous. For thick $SiO_2$ layers no measurable intensity is produced by the Ni deposition in the energy range near 89 eV, where elemental Si or silicides[7] normally contribute, indicating that silicide formation does not occur in this case.

At Ni layer thicknesses below 5 Å the intensities of both oxygen-related Auger lines ($SiO_2$ *LVV* and O *KLL*) remain approximately constant, or even increase slightly. An AES line shift in the low-coverage regime could be seen for the Ni *LMM* (at 845 eV) and O *KLL* lines, both shifting to higher energies by about 1 to 1.5 eV. No line shifts were found for higher Ni coverages.

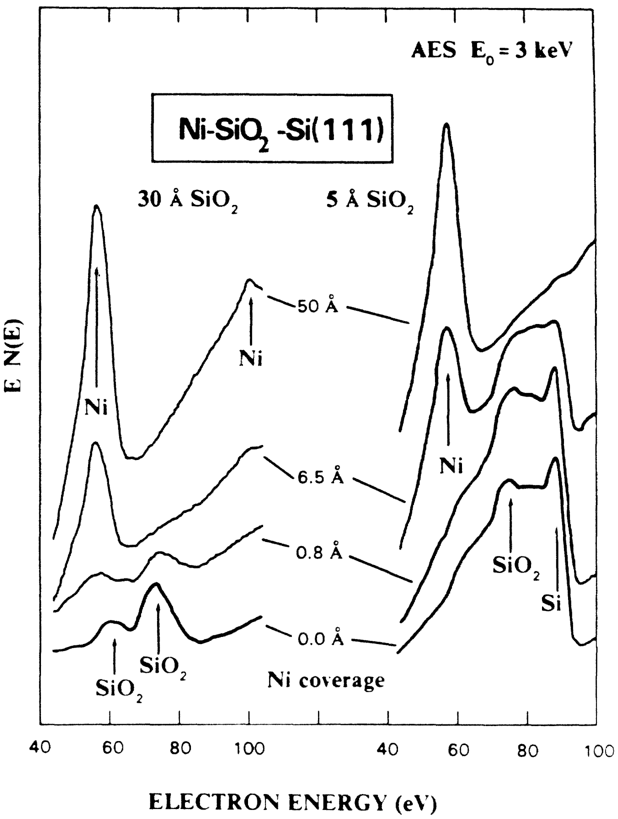

FIG. 1. Auger spectra of the Si *LVV* region for Ni deposition on oxidized silicon (primary energy, 3 keV). The average Ni overlayer thickness ranged from 0.8 to 50 Å. The silicon was oxidized at 1000 °C in a clean oxygen ambient for 1 min. The pressure was 0.1 and $2\times10^4$ Pa for the thin and thick Si oxide, respectively. Thick $SiO_2$: $\sim 30$ Å. Thin $SiO_2$: $\sim 5$ Å. (The oxide thicknesses were estimated from oxide and substrate Auger intensities.)

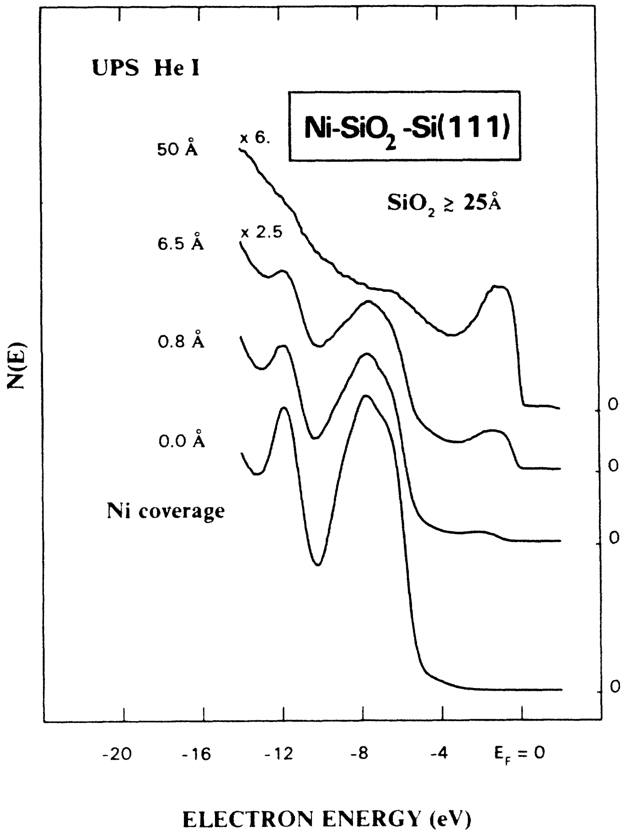

FIG. 2. Ultraviolet photoemission spectra of oxidized silicon covered with Ni layers ranging in thickness from 0.8 to 50 Å. He I light with a photon energy of 21.2 eV was used. The silicon was oxidized at 900 °C in a clean oxygen ambient of $10^3$ Pa for 1 min. (The upper two spectra are magnified.)

Corresponding UPS spectra (He I mode with 21.2 eV photon energy) of a sample with a $SiO_2$ layer thickness $\geq 25$ Å are shown in Fig. 2 (the upper two spectra being magnified as indicated). It was found that for $SiO_2$ layers thicker than ~25 Å, charging effects set in, markedly suppressing the intensity of low-energy electrons. Ni—O bonds are expected[8,9] to produce strong UPS structures at $-5.5$ and $-10$ eV. The absence of such structures (Fig. 2) supports the conclusion that the Ni overlayer does not decompose the $SiO_2$ (to form Ni oxide) at room temperature. This is further supported by previously published results: Thick Ni layers (2000 Å) were found by RBS not to react with thick $SiO_2$ (2000 Å) up to temperatures of 800 °C.[10] This lack of reactivity is also expected from the thermodynamic data for $SiO_2$; for all known silicides and oxides of Ni, a positive heat of reaction is expected for the decomposition of $SiO_2$, ranging from $+6.6$ to $+24.2$ kcal/g atom.

From these considerations it is clear that any reaction between Ni and the underlying Si oxide must be restricted to the first few monolayers, at which the composition sensitivity of AES is insufficient to clearly discern reaction. The photoemission spectra indicate no Ni—O bond formation in the first three monolayers. The observed AES line shifts might be taken as suggesting that reaction has occurred, but it is difficult to distinguish between Ni oxidation and Ni aggregation at these low coverages. SEM examinations show Ni aggregation to occur in ultrathin as-deposited Ni layers on $SiO_2$-covered Si. Such aggregation results in line shifts in x-ray photoemission spectroscopy.[10,11] Finally, the high Ni-atom mobility during annealing, producing agglomeration observed by electron microscopy (and further discussed in the next section), suggests that there is no strong chemical bond between Ni and $SiO_2$.

As seen in Fig. 2, two structures dominate the He I UPS spectrum of oxidized silicon. The more intense peak near $-8$ eV is attributed mainly to an overlap of two nonbonding oxygen $p$ orbitals, whereas the peak at $-12$ eV belongs to a band of bonding $2p$ silicon-oxygen orbitals.[12,13] At low coverage (~2–3 Å), both decrease with Ni coverage more rapidly than expected from the UPS escape depth values (relative to the true secondary peak). We believe that this initial faster decrease is associated with alterations in electron trajectories and collection efficiencies due to microfields generated either by charging of metal islands, oxide patches between islands, or by enhanced electron space charge just above the oxide due to its high secondary-electron yield.[14,15] This kind of interpretation would be consistent with our findings that the rapid initial UPS peak intensity decrease depends on the surface roughness, being more pronounced on smooth surfaces, and that the total secondary-electron yield as measured by the analyzer decreases markedly.

## MORPHOLOGY CHANGES WITH ANNEALING

SEM examinations of heat-treated Ni films reveal a complex microstructure (Fig. 3). The Ni layer on top of the oxide film agglomerates into islands of ~2000 Å average diameter, upon annealing to 750 °C [Fig. 3(a)]. The agglomeration was found to occur for all $SiO_2$ thicknesses used. Annealing above 800 °C caused the Ni layer to penetrate through a 50-Å-thick oxide layer at isolated points on the surface [Fig. 3(b)]. Ni aggregation on $SiO_2$ after heat treatment has been reported for thick oxide layers.[10] For thin oxides, the resulting Ni islands may cluster on top of "weak spots" in the oxide layer,[16,17] where a chemical interaction with the substrate may occur, insuring better local adhesion.

Cross-sectional TEM studies for an 80-Å-thick Ni overlayer on a thick (~30 Å) oxide substrate annealed to 750 °C also show aggregation and formation of metal islands on the oxide surface [Fig. 4(a)]. Electron diffraction revealed that the islands consist of elemental Ni. No direct connection between the Ni islands and the underlying Si can be seen. Moiré patterns, observed at the single-crystal Ni islands [Fig. 4(b)], indicate the presence of a second crystalline phase on or in these islands which has a different structure or orientation than the elemental Ni in the islands. Evidence discussed below indicates that this second phase exists on the surfaces of the Ni islands.

Auger spectra in the vicinity of Si *LVV* are shown in Fig. 5 for such samples. Two oxide thicknesses were used: 50 and 30 Å. They both were overlaid by an ~50-Å-thick Ni layer, deposited at room temperature and subsequently annealed; the former to 500 and 900 °C the latter

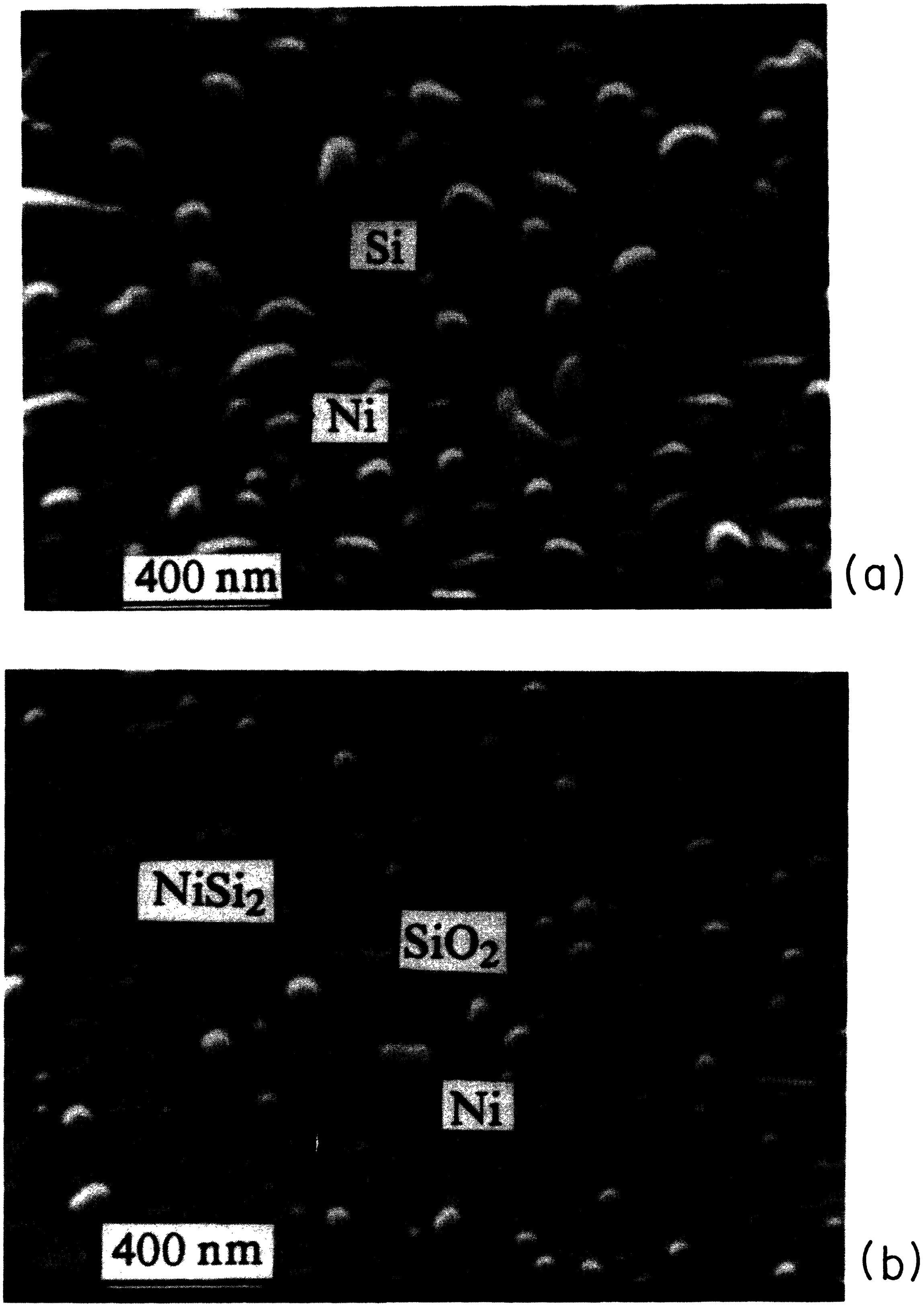

FIG. 3. SEM micrographs of a 75-Å-thick Ni layer on oxidized silicon after annealing to (a) 750 °C, and (b) 900 °C. [The silicon was oxidized in $10^3$ Pa oxygen for 1 min at 900 and 1000 °C for (a) and (b), respectively.] (a) Ni agglomeration into islands upon annealing; (b) Ni penetration through the oxide, upon further annealing, results in NiSi$_2$ formation.

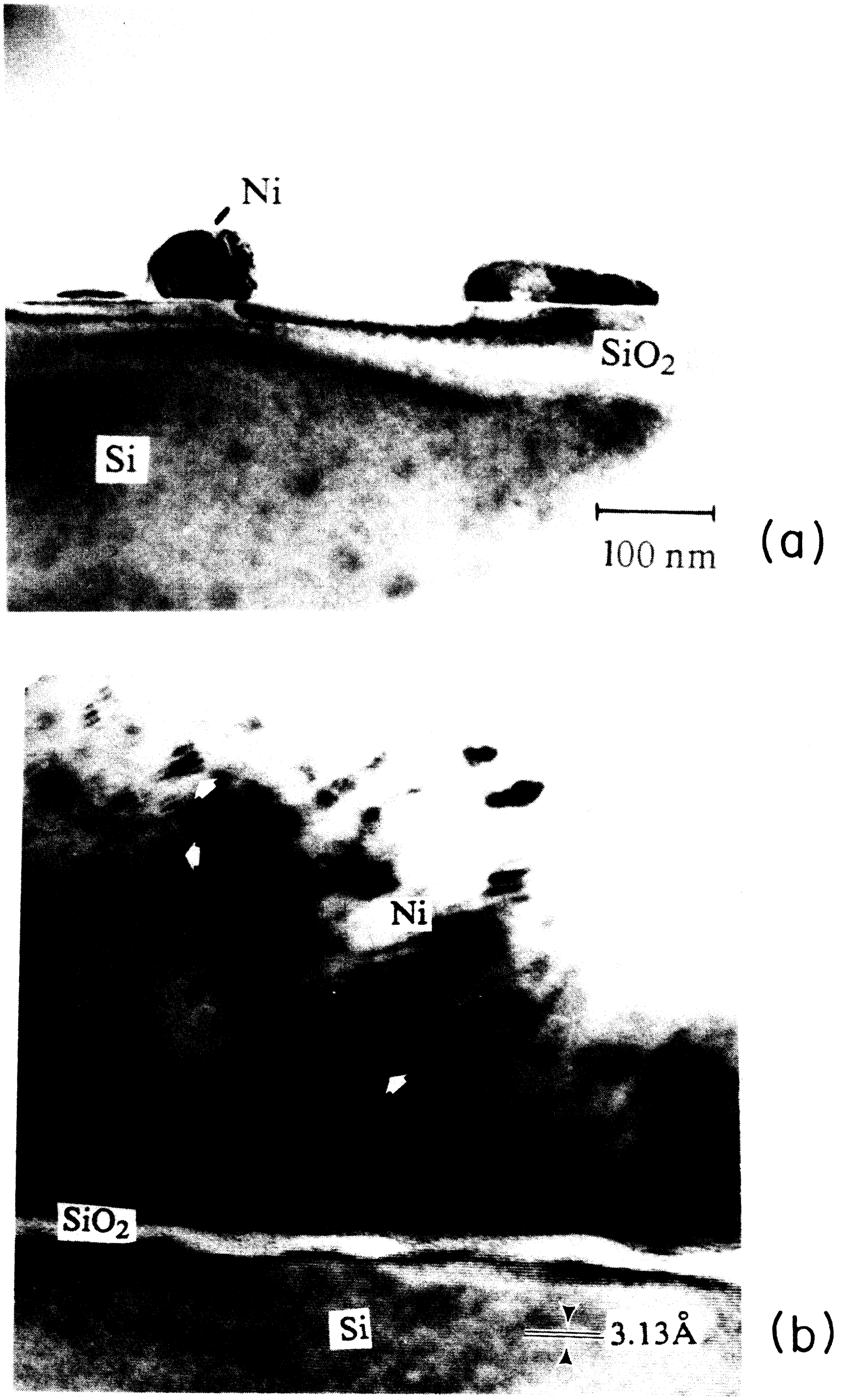

FIG. 4. Cross-sectional TEM micrographs of a 75-Å-thick Ni layer on oxidized silicon after annealing to 750 °C for 10 sec. (The silicon was oxidized at 900 °C and $10^3$ Pa oxygen for 1 min.) (a) Ni agglomerated to form single-crystal Ni islands; (b) Moiré patterns on a Ni island surface.

to 900 °C. Since the Ni overlayer was relatively thick, providing complete coverage of the oxide substrate upon deposition, no Si *LVV* intensity was observed before annealing. The appearance of intensity in the region of the $SiO_2$ *LVV* line upon annealing does therefore indicate a change in the morphology of the Ni layer, exposing areas of bare $SiO_2$. Annealing to 500 °C causes Ni aggregation and island formation. Similar results were found for thinner (~3 Å) and thicker (~70 Å) Ni layers. Since the spectra show no evidence of Si *LVV* intensity at the position expected for Ni silicides (~90 eV), we conclude that little, if any, silicide formation has occurred (the Ni has certainly not been consumed by silicide). This suggests that the Ni-Si reaction, which occurs even at room temperature for clean interfaces,[18] is markedly inhibited by the presence of thin $SiO_2$ layers at the interface. The temperature at which a reaction through the $SiO_2$ begins depends very strongly on the oxide layer thickness, occurring at lower temperatures for thinner oxides and thinner Ni layers (Fig. 5).

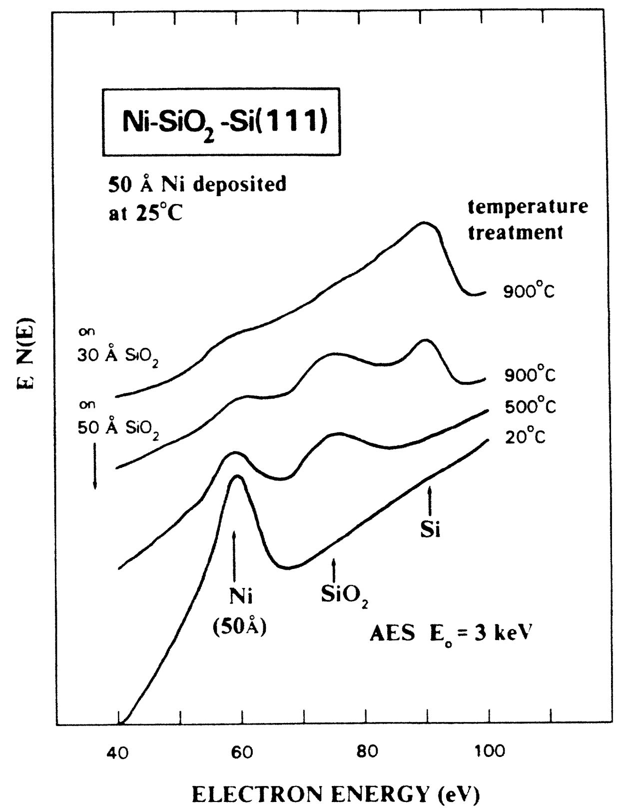

FIG. 5. Auger spectra of the Si *LVV* region for Ni deposited on oxidized silicon (primary energy, 3 keV). The lower three curves are for a 50-Å-thick Ni layer deposited on thick $SiO_2$ at room temperature: as deposited and after annealing to 500 and 900 °C (for 1 min.), respectively. The silicon was oxidized at 1050 °C in a clean oxygen ambient of $10^4$ Pa for 1 min. The upper curve is for a 50-Å-thick Ni layer on a thinner oxide, which was prepared at 1000 °C in $10^3$ Pa oxygen for 1 min.

Although chemical interaction between Ni and $SiO_2$ is very limited, it may not be totally absent. For thicker Ni coverages (≥50 Å), UPS revealed the existence of some oxygen at the Ni-vacuum interface during annealing to 300 °C (Fig. 6: see −6-eV peak). This appears not to be a consequence of oxygen surface contamination from the residual gas. $SiO_2$ decomposition at this temperature, at least on thermodynamics grounds, is rather unlikely. However, it is conceivable that a limited amount of oxygen may be liberated from pinhole areas and other structural defect sites where silicide formation would take place. Such small quantities of oxygen are only detectable in the case of thicker, continuous Ni coverages, because thin Ni coverages cause Ni island formation and the signal due to oxygen is obscured by the presence of the much stronger $SiO_2$ signal.

## HIGH-TEMPERATURE Ni-$SiO_2$-Si REACTION

At low temperatures, and especially for thicker oxide layers, no chemical interaction takes place between Ni and the Si substrate if the $SiO_2$ is continuous, thereby preventing any direct Ni-Si contact. This lack of chemical interaction in Ni-$SiO_2$ (for $SiO_2$ thickness ≥20 Å) does still persist for temperatures up to ~800 °C.

The dominant reaction at elevated temperatures is the formation of silicide, as distinguished by the characteristic

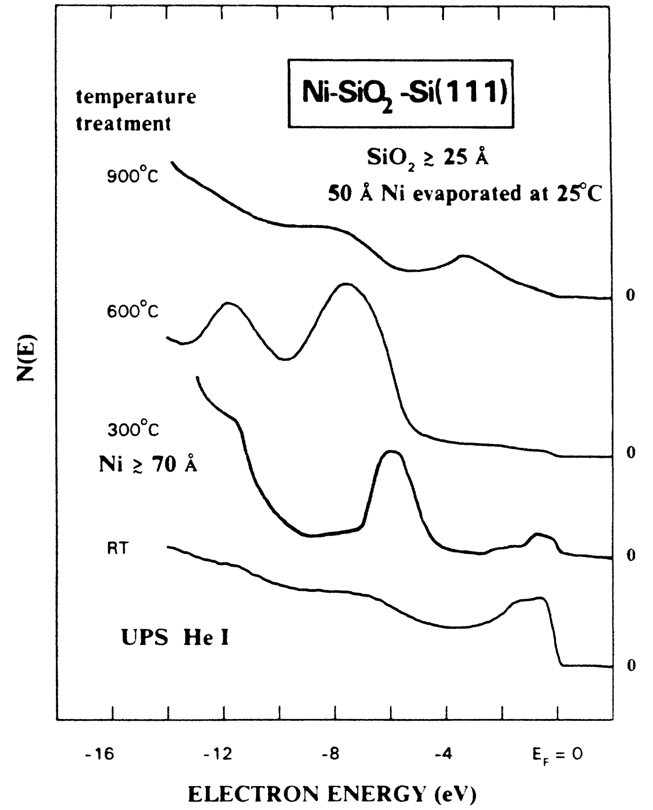

FIG. 6. Ultraviolet photoemission spectra of oxidized silicon covered with Ni layers of 75 Å (second lowest) and 50 Å. He I light with a photon energy of 21.2 eV was used. The silicon was oxidized at 1000 °C in a clean oxygen ambient of 0.1 Pa for 1 min. The indicated heat treatments had a duration of 1 min. each.

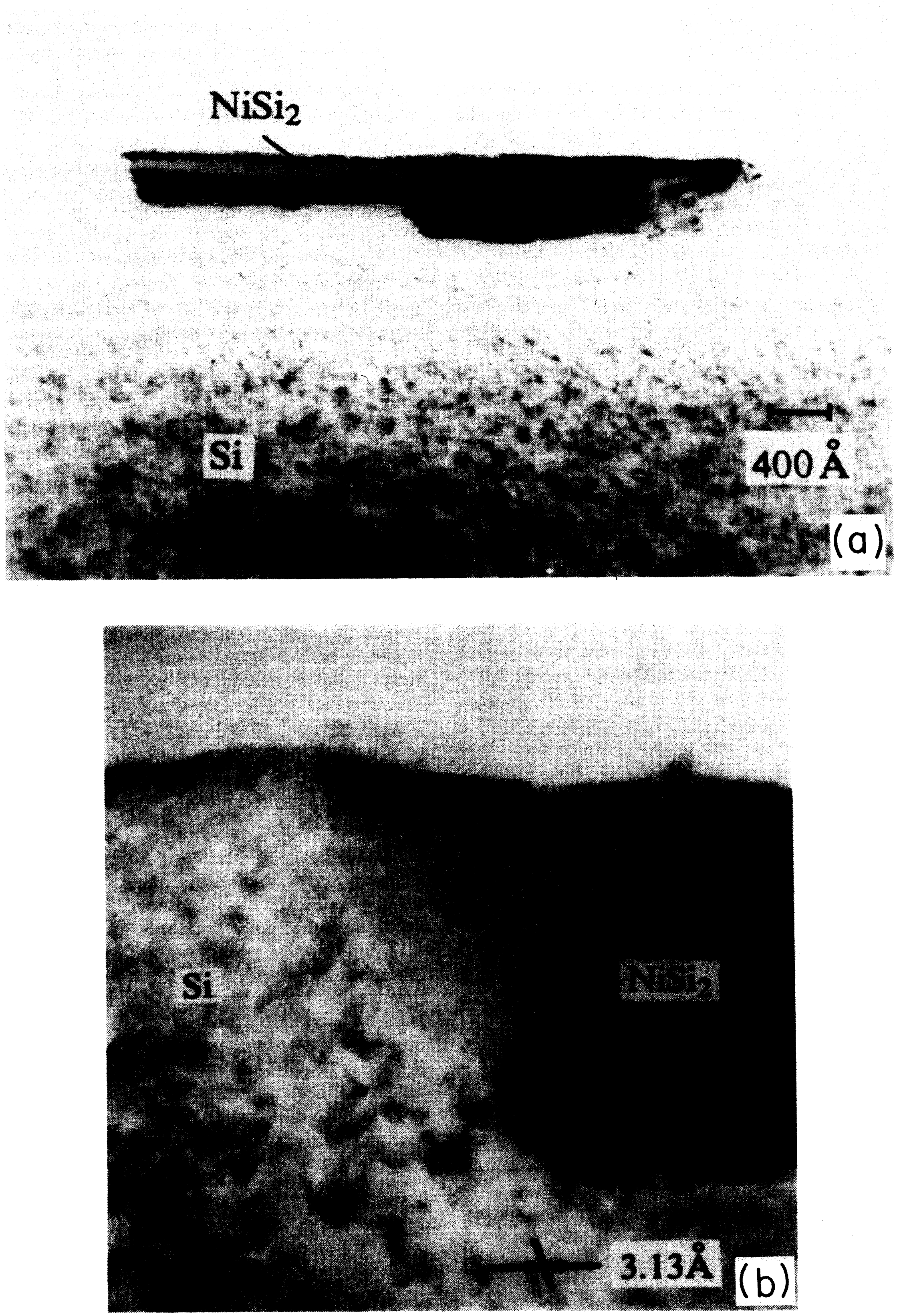

FIG. 7. (a) and (b): Cross-sectional TEM micrographs of epitaxial $NiSi_2$ islands formed by annealing the structure 50-Å Ni/50-Å $SiO_2$/Si to 900 °C for 1 min. (The $SiO_2$ was formed by heating the Si substrate to 1000 °C and in $10^3$ Pa oxygen for 1 min.)

silicide features in the Si *LVV* Auger spectrum. For oxides $\leq 20$ Å thick, this reaction occurs at temperatures well below the decomposition temperature of thin $SiO_2$ on Si ($\leq 800\,^{\circ}C$) (Ref. 19) and therefore the interpretation of the silicide *LVV* line is unambiguous. At temperatures $\geq 800\,^{\circ}C$ (necessary to cause a reaction through a $SiO_2$ layer $\geq 20$ Å thick), AES alone is no longer able to unequivocally follow the reaction, as it cannot distinguish between silicide growth and $SiO_2$ decomposition. The formation of silicide islands is only revealed by TEM. Indeed, electron diffraction of the high-temperature treated samples (of both thin and thick $SiO_2$ layers) determined the product of the Ni-Si reactions as $NiSi_2$.

The dependence of the Ni-Si reaction on Si-oxide thickness and temperature indicates a diffusion process which does not involve chemical interaction with the oxide. Such material transport would obviously be facilitated by the presence of pinholes (or other structural defects) in the oxide. The exact mechanism of the transformation from Ni islands to a silicide layer is not yet clear. TEM examination revealed the presence of traces of oxide only near the outer surface of the silicide. This suggests that Ni is the dominant moving species in the reaction.[20]

In addition, some silicon transport through pinholes in the oxide must also take place during the early stages of the silicide formation when there still are metal islands above the surface. At the beginning of such treatments, AES revealed silicide growth, whereas TEM showed diffraction patterns of Ni. This discrepancy may be resolved by assuming formation of a silicide surface layer around the Ni islands. While the former is readily seen by AES, the bulk of the metal islands still consists of Ni, producing the TEM diffraction patterns. The existence of such a surface layer can be strongly supported by the TEM Moiré patterns visible on the Ni islands [Fig. 4(b)]. A quite similar behavior has been found for Ni deposition on clean Si.[21]

Cross-sectional TEM was also performed on the same kind of sample heated to 900 °C (Fig. 7). Epitaxial $NiSi_2$ islands were found to have formed, with an average diameter of 2000 Å. The Ni silicide structure was almost entirely of the *A*-type.[3]

At the highest temperatures used here (800–900 °C), a further reaction seems to take place. Both the $SiO_2$ and oxygen peak intensities in UPS and AES diminished strongly after the anneal. TEM showed almost no inclusions of oxide in the growing silicide or at the Si/silicide interface. Since $SiO_2$ on Si is still stable at the temperatures and durations of these anneals, it appears that one of two things must be happening to the oxide. First, it is possible that the presence of silicide, or of Ni atoms somewhere in the structure,[22] reduces the temperature needed for oxide decomposition, as in a catalytic process. Second, it is conceivable (though perhaps unlikely) that the silicide lattice absorbs significant amounts of oxygen in a form (highly microscopic) which is not observable in TEM or AES.

## SCHOTTKY-BARRIER HEIGHT

The Schottky-barrier height after silicide formation was determined by current-voltage (*I-V*) and photoresponse measurements for samples with different initial oxide thicknesses. The barrier values determined by (*I-V*) measurements reflected the agglomeration of the Ni into islands which were electrically isolated from each other. Measurements with a supplementary Ag layer (to reduce the high series resistance of the silicide layer) yielded barrier heights of $0.60\pm0.03$ eV with rather high idealities (between 1.2 and 1.8). Photoresponse measurements without a Ag layer yielded a barrier height of $0.61\pm0.03$ eV.

Similar values were found for rough or polycrystalline Ni silicide/*n*-type Si(111) interfaces in the absence of an interfacial oxide.[23,24] TEM showed that on the oxidized samples large grains of single-crystal epitaxial silicide were formed, separated by regions of bare silicon covered only by the native oxide (probably grown after exposure of the samples to air).

An important feature here is the presence of nearly pure type-*A* $NiSi_2$ (Ref. 3) at the interface of fully reacted samples. The measured barrier height (0.60 eV), however, is different from that of pure type-*A* $NiSi_2$ found using the same preparation conditions but using clean instead of oxidized silicon (0.78 eV). The Schottky-barrier height in the Ni-Si system has been found to critically depend on the microstructure of the interface between silicide and silicon;[4] for slightly imperfect epitaxial quality, the barrier height is decreased to $\sim 0.65$ eV. Since the major influence on the barrier height of these interfaces is the perfection of the interface, the oxide would appear to lower the Schottky-barrier height simply by influencing the long-range epitaxial quality and microstructure (e.g., steps at the interface). The growth of large islands, therefore, though epitaxial, is sufficient to have a dramatic influence on the Schottky-barrier height.

## CONCLUSIONS

The influence of interfacial oxygen or $SiO_2$ on the reactivity of the Ni/Si interface was studied by AES, UPS, SEM, and TEM. No spontaneous interfacial reaction between Ni and Si takes place at room temperature when the $SiO_2$ interlayer is present. Ni aggregates initially into islands but does react with the underlying Si upon subsequent annealing, apparently through pinholes in the $SiO_2$ layer. The reaction product is $NiSi_2$ and the reaction requires higher temperatures for thicker $SiO_2$ layers, suggesting mass transport through the oxide. A small amount of decomposition of the $SiO_2$ may also take place at elevated temperatures and at structural defects such as pinholes in the oxide. Such a reaction promoted by the silicide formation may lead to the rapid, complete decomposition of the oxide at elevated temperatures. A low Schottky-barrier height of $0.60\pm0.04$ eV was found for reacted contacts.

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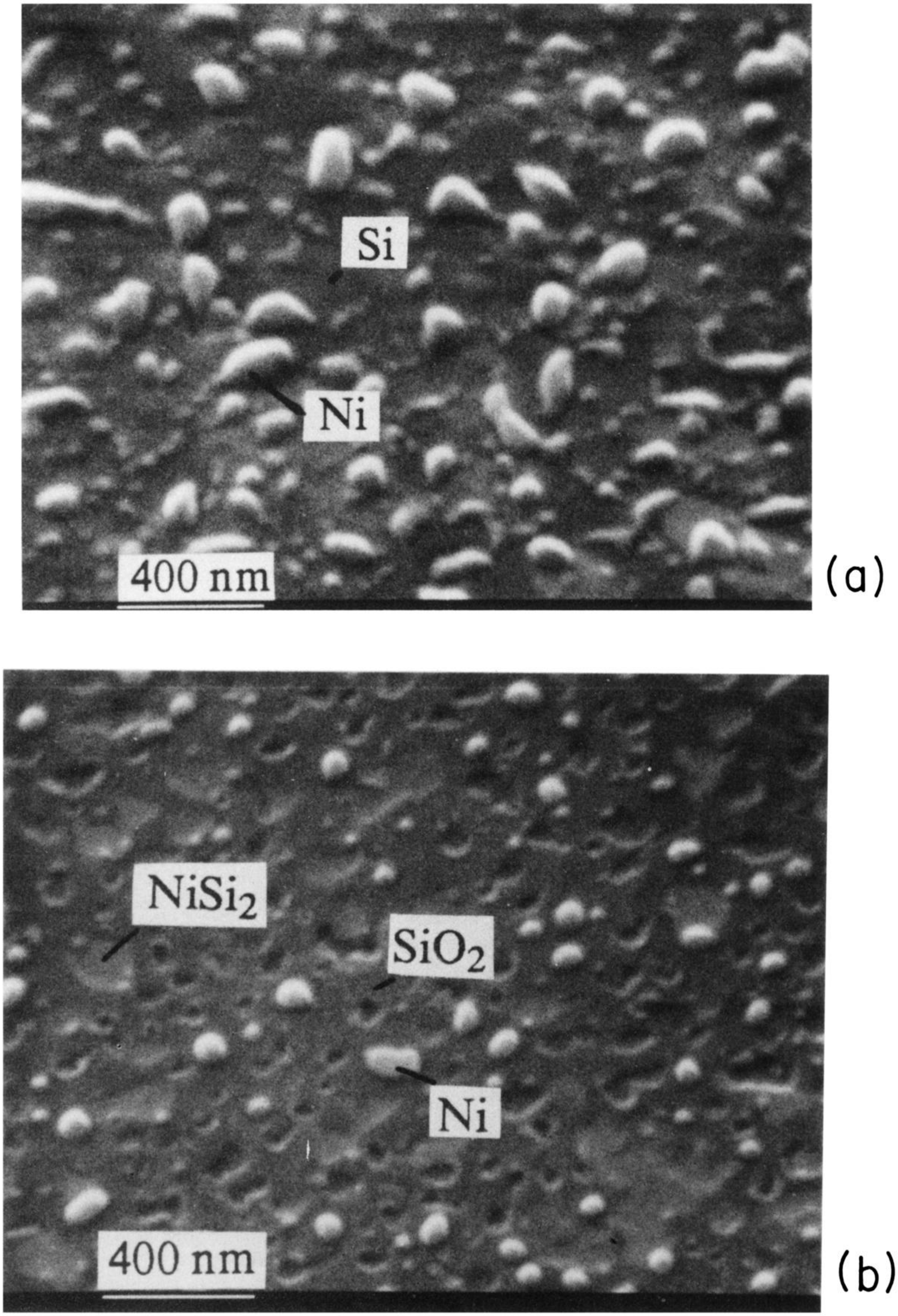

FIG. 3. SEM micrographs of a 75-Å-thick Ni layer on oxidized silicon after annealing to (a) 750 °C, and (b) 900 °C. [The silicon was oxidized in $10^3$ Pa oxygen for 1 min at 900 and 1000 °C for (a) and (b), respectively.] (a) Ni agglomeration into islands upon annealing; (b) Ni penetration through the oxide, upon further annealing, results in $NiSi_2$ formation.

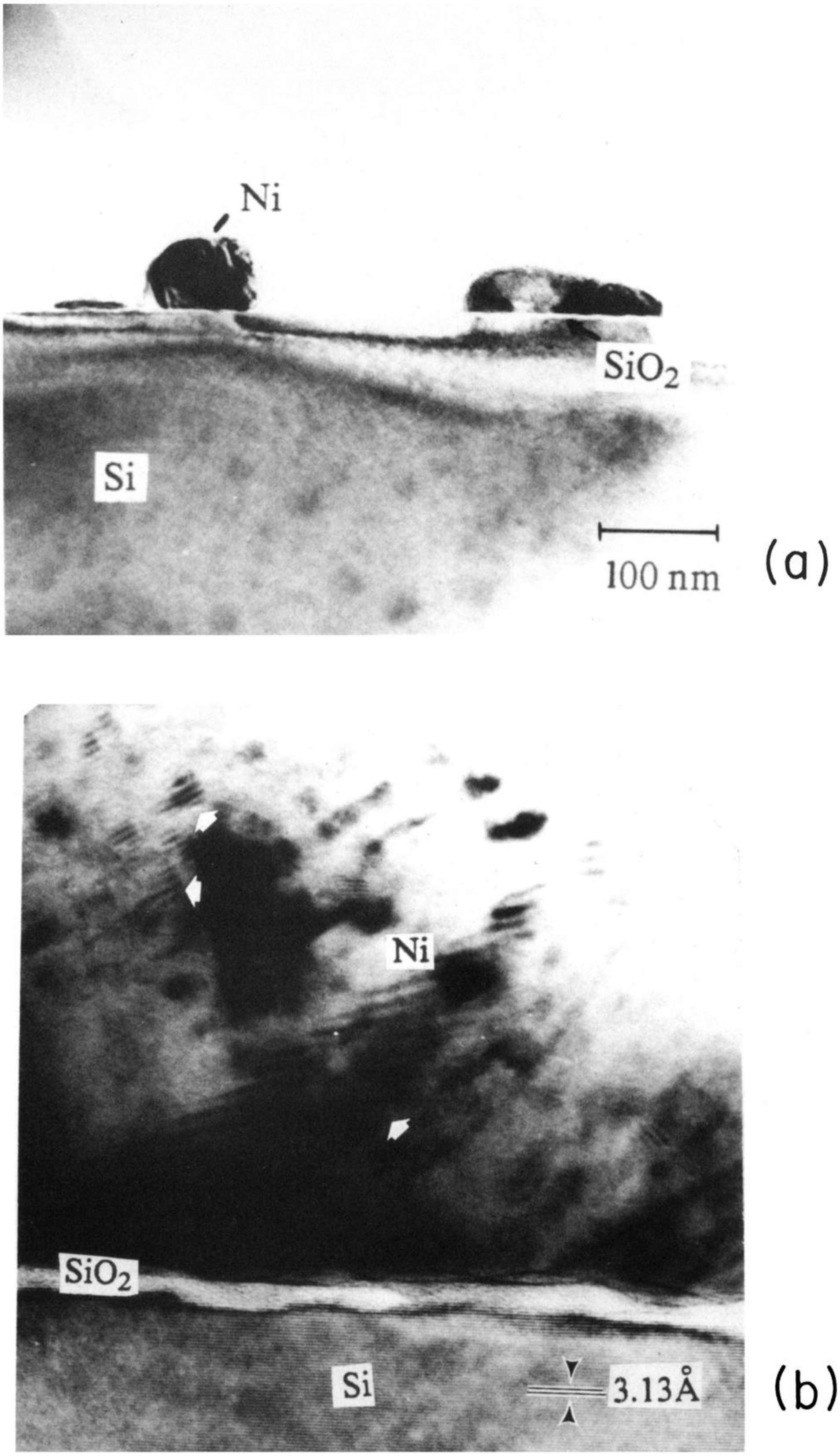

FIG. 4. Cross-sectional TEM micrographs of a 75-Å-thick Ni layer on oxidized silicon after annealing to 750 °C for 10 sec. (The silicon was oxidized at 900 °C and $10^3$ Pa oxygen for 1 min.) (a) Ni agglomerated to form single-crystal Ni islands; (b) Moiré patterns on a Ni island surface.

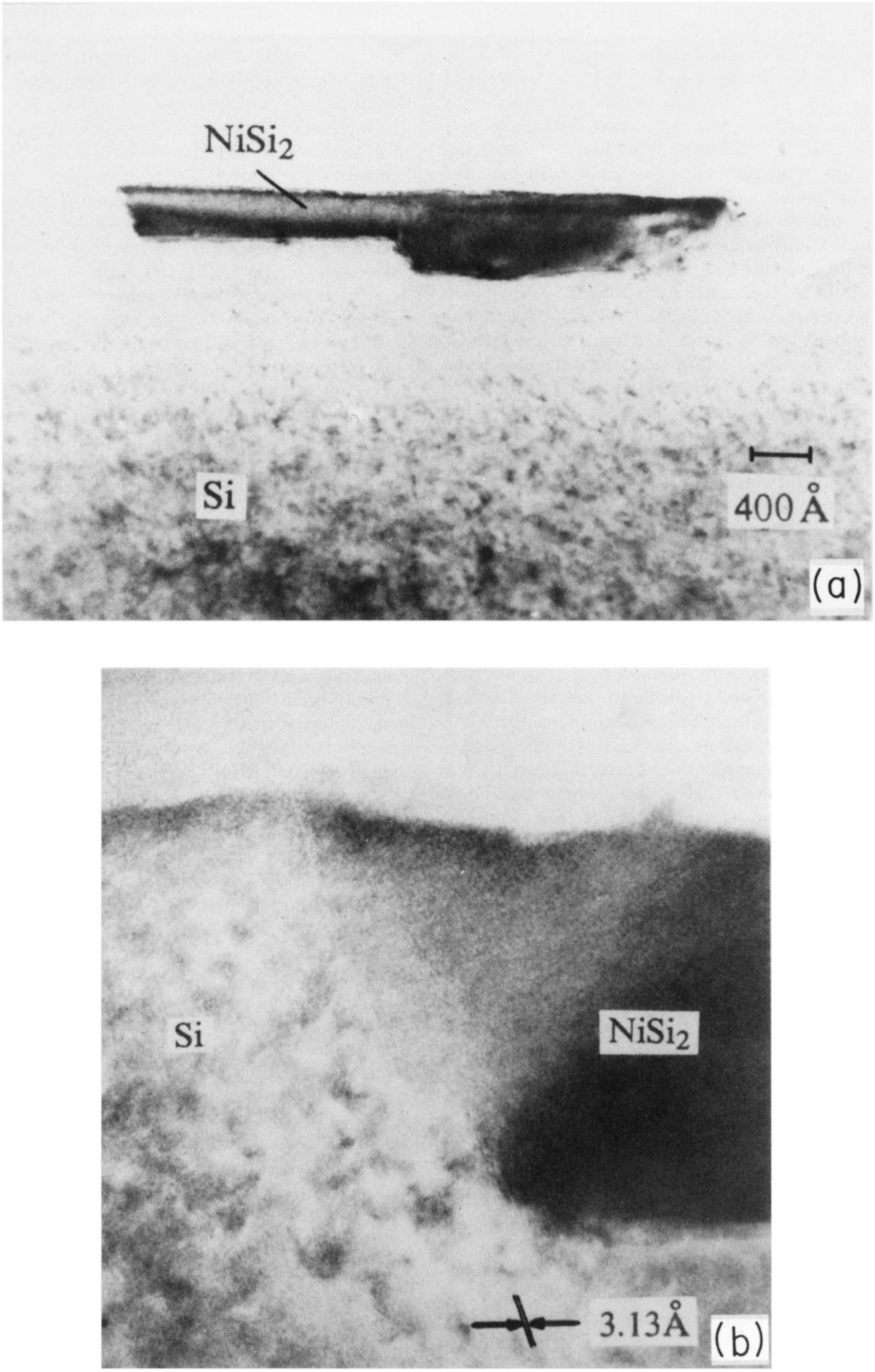

FIG. 7. (a) and (b): Cross-sectional TEM micrographs of epitaxial $NiSi_2$ islands formed by annealing the structure 50-Å Ni/50-Å $SiO_2$/Si to 900 °C for 1 min. (The $SiO_2$ was formed by heating the Si substrate to 1000 °C and in $10^3$ Pa oxygen for 1 min.)