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Chemical and structural aspects of reaction at the Ti/Si interface

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Chemical bonding and reactions at the Ti/Si(111) interface have been studied as a function of Ti overlayer thickness and annealing temperature and time. The chemical properties (composition, electronic structure, and reactivity) were observed under ultrahigh-vacuum conditions using photoemission (ultraviolet and x ray) and Auger electron spectroscopies; the structural properties (phase and microstructure) were investigated by subsequent transmission electron microscopy; sputter-depth profiling was employed to complete the characterization of the material formed by interface reaction. At room temperature the clean Ti/Si interface remains unreacted, i.e., no intermixing of atoms across the interface occurs; this behavior is similar to that of V/Si but in contrast to the more common initial limited reaction (~ 10 Å depth) which takes place for other transition-metal/Si interfaces, especially the near-noble metals. At sufficiently high temperatures ($\geq 600\,^{\circ}$C), growth of the silicides TiSi and $TiSi_2$ takes place over considerable distances (hundreds of angstroms or more) as expected from previous thin-film investigations. However, initial reaction at the interface can occur at temperatures considerably lower ($\sim 300\,^{\circ}$C), and this reaction can extend over a considerable distance (~ 100 Å or more) from the Si interface. This low-temperature intermixing process leads to structural properties quite different from those induced by silicide compound formation at higher temperatures: The reacted material forms Ti-Si mixtures with very small grains (~ 10–30 Å in size), if not nearly amorphous material. Finally, if the low-temperature reaction has already progressed considerably, the kinetics of transformation to well-defined larger grain silicide phases is altered, and notably higher reaction temperatures are required to reach the same structural state. These observations suggest the possibility that the phase kinetics and microstructure associated with the Ti/Si interfacial reaction can be altered in the intermediate reaction stage observed at low reaction temperatures.

I. INTRODUCTION

Despite the considerable body of research which has been carried out over the past few years on transition-metal/Si and corresponding silicide/Si interfaces,[1–15] only a small fraction of these studies have addressed the refractory transition metals.[6–17] This situation is unfortunate because it limits the overall view of the chemical trends involved in reactions at the transition-metal Si interface. It represents a problem to technology as well. because the needs of Si bipolar device technology include low-barrier contacts (Schottky barrier heights that are ≤ 0.65 eV to *n*-type Si), which the refractory transition metals and their silicides can provide.

Previous thin-film investigations have shown that bulk silicide films can be grown by contact reaction at the Ti/Si interface for temperatures $\geq 500\,^{\circ}$C;[18–22] TiSi forms initially, but at higher temperatures ($\sim 650\,^{\circ}$C) the final phase $TiSi_2$ is produced. The present work addresses the basic properties and reactions at the Ti/Si interface on a microscopic level, i.e., with sensitivity on the atomic scale. Furthermore, it provides a considerably more complete picture of *both* the chemical and structural properties of the interface region than was available from previous surface or interface spectroscopy studies.[7,8,14] The results demonstrate the strongly reactive character of such interfaces. It also shows clearly that the *nature* of interface chemical reaction for this refractory, as for V and in some ways for Cr, is quite different than for near-noble transition metals. First, the spontaneous initial silicide formation (to ~ 10 Å metal coverage) which was surprising yet characteristic of the near-noble metals is not detected here. Nevertheless, reaction at atomically clean interfaces does begin well below the temperatures where formation of silicides is observed at less clean interfaces. The nature of this low-temperature reaction at the interface has been clarified by microstructure examination, which indicates an initial stage of formation of the TiSi and $TiSi_2$ phases. Coupling with the reaction at the interface, mass transport occurs over considerable distances from the Si interface (hundreds of angstroms) to form a silicon-rich mixed overlayer. Results of this study demonstrate the importance of combining structural and chemical information for clarifying properly the characteristics of the interfacial reaction, particularly for a relatively complex system such as the Ti/Si interface.

II. EXPERIMENTAL TECHNIQUES

To understand the reactive chemistry and properties of the Ti/Si interface, a variety of experimental techniques was used. Both ultraviolet (UPS) and x-ray (XPS) photoemission spectroscopy and Auger electron spectroscopy (AES) were employed to determine interface electronic structure, composition, and reactivity. The composition in depth of the overlayer was further investigated by sputter-profiling techniques. The lattice structure, crystalline phases, and microstructure were analyzed by transmission electron microscopy (TEM) studies on samples after removal from vacuum. Low-energy electron diffraction (LEED) was employed to check long-range surface order.

The surface spectroscopy experiments (UPS, AES, XPS) were made in a UHV (ultrahigh vacuum) chamber with an operating pressure $\sim(1-2)\times10^{-10}$ Torr, using a large ($\sim$10-in.-o.d.) double-pass cylindrical mirror analyzer to measure electron kinetic energies and an internal 8-keV electron gun as an electron source for AES. Other facilities included a differentially pumped rare gas discharge lamp to produce ultraviolet light for UPS, a twin-anode differentially pumped x-ray source for XPS, a sputter-ion gun for sputter cleaning the sample *in situ*, and evaporation sources for *in situ* deposition of metal overlayers.

Si samples were prepared from *n*-type wafers (10 Ω cm, 0.010 in. thick) with [111] orientation. To achieve uniform and reproducible sample heating both for annealing after sputter cleaning and for thermal processing of the interface, a Ta layer $\sim$1000—2000 Å thick was first deposited on the back side of the wafers. The wafers were then cut into rectangular shapes 0.75×0.25 in.^{2}, and clearance holes were ultrasonically drilled in each end of the samples to accommodate Ta screw-and-nut assemblies used as high-temperature mechanical contacts. Ta wires (0.015 in. diam.) were spot welded to these assemblies to mechanically support the samples, which could thus be annealed to $\geq$1000 °C by direct resistive heating. With this arrangement, uniform heating to within $\sim\pm50$ °C was attained even at high temperatures over the entire region ($\sim0.25\times0.40$ in.^{2}) between the screws, and the electrical resistance of the sample package was quite reproducible. The temperature of the sample was monitored by a chromel-alumel thermocouple spot welded to one of the Ta screw contacts, and the actual sample temperature was then calibrated with an infrared pyrometer for temperatures $\sim$150 °C or above.

The Si sample surfaces were cleaned by *in situ* Ar$^+$ sputtering (500 eV) and consequent annealing to $\sim$900 °C to restore the ordered crystal structure of the surface. For the Si(111) surface this gave the well-known Si(111)-(7×7) LEED structure.

Depositions of Ti metal overlayers were carried out with the sample surface in the measurement position used for UPS, AES, and XPS, so that accurate comparison of relative intensities of various spectral features could be made as a function of both metal coverage and annealing. Evaporation was from a Marz grade (99.999% purity) Ti slug held in a Ta holder which was heated by electron bombardment. This source was located in an isolatable, separately pumped evaporation chamber in direct line-of-sight to the sample measurement position, as described elsewhere.[6] Differential pumping of the source is achieved by the presence of a low-conductance line-of-sight tube between the evaporation chamber and the measurement chamber; as a result of this differential pumping, the pressure at the sample does not increase (on the 10^{-10} Torr scale) even though outgassing of surfaces near the high-temperature source is appreciable. Deposition rates at the sample were of order 1 Å/min. A quartz-crystal monitor in the evaporation chamber is used to measure the evaporant flux, which is then corrected for geometric factors involving source-monitor and source-sample distances and angles.

In spite of the advantages of the differentially pumped evaporation chamber, small amounts of oxygen contamination ($\sim\frac{1}{4}$ monolayer) were observed at higher Ti coverage ($\geq$5 Å) by UPS, even though AES and XPS showed no evidence of this oxygen. This small amount of contamination was surprising, since no such oxygen contamination was observed even in UPS in previous experience with another high-temperature refractory metal [V (Ref. 6)]. Some time after the Ti/Si experiments were completed, a small leak was found in the evaporation chamber which may have caused its slightly elevated base pressure ($\sim1\times10^{-9}$ Torr) and the oxygen contamination (the leak was in the ion pump between the outside water jacket and the inside of the pump chamber). Unfortunately, the UPS cross section for oxygen is very high, so that the UPS measurements show clear structure from the oxygen contamination. Nevertheless, the conclusions reached here are independent of the presence of this small amount of oxygen on the Ti overlayer surface.

III. INTERFACE PROPERTIES AND REACTION

To understand the chemistry and properties of the *interface* between Si and the metallic overlayer (whether pure Ti metal or a Ti-Si reaction product), we first concentrate on the results for relatively low Ti coverage. The composition of the overlayer formed by a sequence of Ti depositions is shown in Fig. 1. For room-temperature deposition, the Si $L_{2,3}VV$ AES intensity decays exponentially with coverage as expected if the Ti forms a pure metal layer which covers the Si substrate and thus attenuates the Si signal (with a reasonable Si $L_{2,3}VV$ escape depth $\sim$9 Å). Since no intermixing of Ti and Si atoms

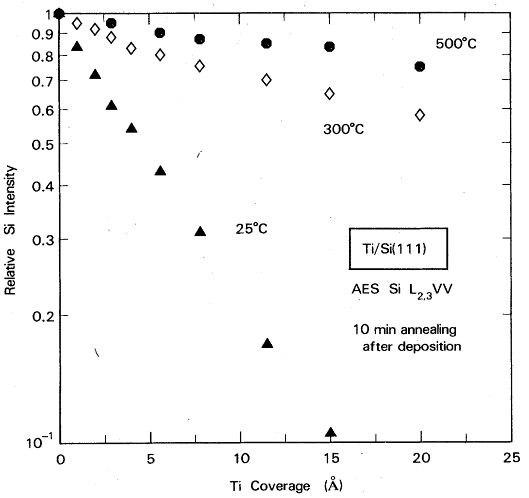

FIG. 1. AES intensity behavior of Si $L_{2,3}VV$ as a function of Ti coverage at various temperatures. For the 300- and 500-°C cases, each data point corresponds to depositing more Ti at room temperature, annealing for 3 min at the elevated temperature, and remeasuring the intensity at room temperature.

across the Ti/Si interface seems to have occurred, we refer to the interface and/or overlayer as *unreacted.*

We thus conclude from compositional evidence that the Ti/Si interface remains *unreacted* at room temperature. This situation is similar to the case of V/Si (Ref. 6) but is in contrast to the cases of most other transitions metals (e.g., Pd, Pt, etc.), where an initial thin (≤ 10–15 Å) silicide layer is formed spontaneously at room temperature or even lower.

At higher temperatures substantial intermixing or reaction takes place at the interface, as also seen in Fig. 1. For successive Ti depositions, each of which is followed by a 10-min annealing cycle, the Si intensity decays much more slowly with coverage than in the unreacted room-temperature case. This is a clear indication that Si is present near the surface of the overlayer, not just in the original substrate. As illustrated in the 300- and 500-°C results in Fig. 1, the amount of intermixing is greater at higher temperatures.

Corresponding information about the distribution of the Ti in depth is shown by the results in Fig. 2. Here the intensities of the Ti $L_{2,3}M_{2,3}M_{2,3}$ AES transitions are shown as a function of annealing temperature for various Ti coverages, where again the annealing times were 3 min each. The marked decrease of Ti intensity upon annealing to $\geq 300\,^{\circ}\mathrm{C}$, observed for all coverages, is attributed to initial Ti-Si reaction at the original Ti/Si interface, which thus decreases the amount of Ti present within the sampling depth at the overlayer surface (~ 15–20 Å for Ti $L_{2,3}M_{2,3}M_{2,3}$). Although this decrease in Ti signal could in principle be explained as well by agglomeration of Ti on top of the Si surface, this explanation is ruled out by AES sputter profiling and TEM structural observations; these results and clarification of the nature of the interfacial reaction will be given below.

UPS spectra for the deposition of thin layers of Ti at room temperature are shown in Fig. 3. The spectrum for the clean Si(111) surface shows bulk Si peaks near -7 and -3.5 eV and intrinsic surface-state features[22] near -1.8 and -0.9 eV. Upon Ti deposition, the intrinsic surface states are quenched and the bulk Si features are attenuated; at the same time, new features appear even at 2.2 Å, particularly just below the Fermi energy E_F. At 6.0-Å coverage, two main peaks are prominent. The peak just below E_F is similar to that expected for the $3d$-derived band of pure Ti metal, because the Ti($3d$) bands are mainly empty (the Ti atomic configuration is d^2). The additional peak near -6 eV is characteristic of chemisorbed oxygen [i.e., O($2p$) states].[7] With increasing Ti coverage the Ti($3d$) peak develops an asymmetric shape, with a sharp cutoff at E_F, while the amount of oxygen on the Ti surface increases and the oxygen-derived structure splits into two peaks.

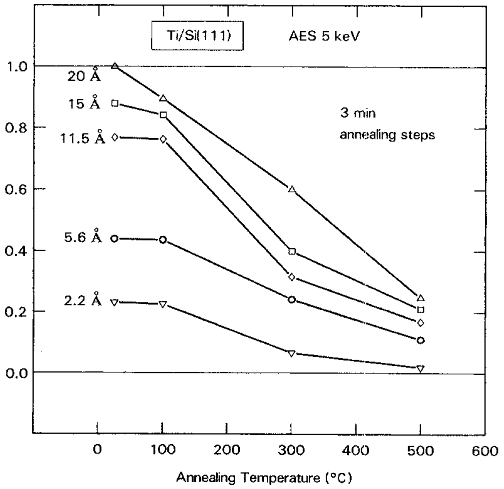

FIG. 2. AES intensity behavior of Ti $L_{2,3}M_{2,3}M_{2,3}$ as a function of annealing temperature for various coverages. Annealing times were 3 min each.

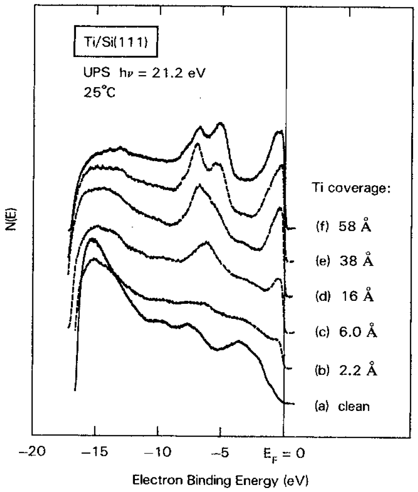

FIG. 3. UPS ($h\nu=21.2$ eV) spectra for (a) clean Si(111) and (b)–(f) increasing Ti coverage, all at room temperature. The peak which evolves just below the Fermi energy is the occupied Ti($3d$)-derived band, while the structure near -6 eV results from submonolayer oxygen contamination on the Ti surface at higher coverages.

In principle one would like to use the low-coverage deposition results in Fig. 3 to determine whether the interface electronic structure reflects silicidelike bonding features, as done previously for both near-noble and refractory transition metals.[1,5] However, differences between the UPS spectrum of bulk $TiSi_2$ (Ref. 14) and that of bulk Ti metal (as represented by the 58-Å spectrum in Fig. 3) are fairly small: For $TiSi_2$ the Ti($3d$) peak is located at -1 eV, while for pure Ti it occurs closer to E_F just as the Fermi cutoff which separates occupied and unoccupied electronic states. These differences are considerably smaller than those between VSi_2 and bulk V metal.[6] The oxygen-contamination structure at ≤ -5 eV in Fig. 3 does not make it more difficult to differentiate between silicide and pure metal, at least as judged by the comparison between VSi_2 and V.

Views of the valence electronic structure of the interface can also be obtained from the bandlike Si $L_{2,3}VV$ AES transition. These spectra have been extremely useful for near-noble transition-metal/Si interfaces and their interfaces[23,24,4] because they differ quite considerably from those of pure Si. However, the Si $L_{2,3}VV$ spectra for refractory transition-metal silicides are very similar[6,25] to those of pure Si and thus give little information about changes in the bonding of the Si atoms, a fact we also found to be true from the present Ti/Si studies. The similarity between refractory silicide and pure Si $L_{2,3}VV$ spectra arises primarily because the group of antibonding silicide states are located above the Fermi energy: They are therefore unoccupied and cannot influence the spectral features observed in the Si $L_{2,3}VV$ AES transition.

Thus we conclude that it is difficult to distinguish between silicidelike (Ti-Si) and pure-metal (Ti) bonding on the basis of the interface electronic structure as seen in UPS and AES spectra in the interface (low-coverage) region. Instead, we infer that the interface is unreacted at room temperature from composition analyses like those in Figs. 1 and 2.

IV. CHEMICAL PROPERTIES OF REACTED Ti-Si OVERLAYERS

We now turn to the question of how the interface chemical reaction proceeds and the chemical characteristics of the resulting reacted overlayers. A useful view of the reactivity is obtained from surface spectroscopy studies of the top region of a thicker Ti overlayer, as demonstrated by the results in Fig. 4, which shows the temperature dependence of the Si AES intensities for a thicker (75-Å) Ti film as compared to that for a thinner (5-Å) film. As can already be seen for the 5-Å film, annealing 300 and 500 °C increases the Si $L_{2,3}VV$ signal. At 25 °C the 75-Å unreacted Ti film completely quenches the signal from the underlying Si substrate. Upon annealing to 300 °C, the Si $L_{2,3}VV$ signal increases notably. The appearance of the Si signal upon annealing demonstrates very clearly that some kind of Ti-Si intermixing has taken place over a considerable distance from the initial Ti/Si interface. This increase is much smaller as seen by the Si *KLL* signal. Since the electron escape depth of the Si $L_{2,3}VV$ transition (~ 8 Å) is considerably shorter than that of the Si *KLL* transition (~ 20 Å),[6] we conclude that the Si which is present in the overlayer due to 300 °C annealing is concentrated primarily in the top region of the film: If the overlayer composition were homogeneous in depth, the relative intensities of the Si $L_{2,3}VV$ and *KLL* transitions in Fig. 4 would be the same.

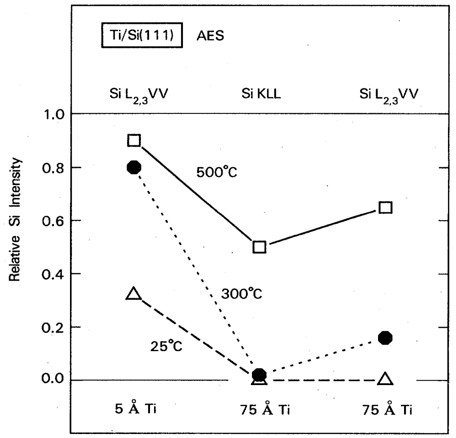

FIG. 4. AES intensity behavior of Si $L_{2,3}VV$ and *KLL* for a fairly thick (75-Å) Ti film as a function of annealing temperature (10 min treatments) and as compared to a thin (5-Å) film.

With annealing to higher temperature (500 °C), the Si content increases to over 50%, as would be expected for silicide compound formation. Furthermore, the Si $L_{2,3}VV$ and *KLL* intensities become more nearly the same, suggesting a more uniform composition distribution in depth for the reacted overlayer.

A more complete determination of the effect of annealing treatments on overlayer surface composition is given in Fig. 5. The results are expressed in terms of the partial Ti composition in the overlayer film. Since the film is thick compared to the escape depths for the Si transitions, the overlayer surface appears as pure Ti when the film is unreacted, which is the situation below ~ 250 °C. With annealing to ≥ 250 °C, however, the Ti concentration decreases, indicating an increase in Si concentration in the top portion of the overlayer. At intermediate temperatures (~ 250—300 °C), the overlayer composition is nonuniform in depth: It is more Si rich near the top surface since the Si $L_{2,3}VV$ transition (short escape depth) indicates a higher Si intensity than does the Si *KLL* or Ti $L_{2,3}M_{2,3}M_{2,3}$ transition.

At higher temperatures (500 and 650 °C) more typical of Ti silicide growth, the composition approaches that of $TiSi_2$, as if one is observing a straightforward silicide compound formation process as expected from thin-film literature. Thus the results of the intensity analysis show that for a thicker film (~ 100 Å), reaction at the clean Ti/Si interface already begins at ~ 250 °C; this reaction involves Si diffusion over a considerable distance (~ 100 Å) from the initial interface.

To better assess the composition of the overlayer in depth, AES sputter-profiling experiments were carried out on Ti overlayers 90 Å thick using Ar^+ ions at the same flux. These results are given in Fig. 6. Here both Ti $L_{2,3}M_{2,3}M_{2,3}$ and Si $L_{2,3}VV$ AES transition intensities were used to determine the composition, which is ex-

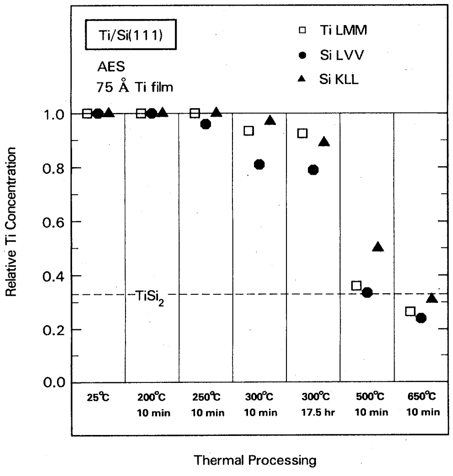

FIG. 5. AES intensity behavior of Si $L_{2,3}VV$, Si *KLL*, and Ti $L_{2,3}M_{2,3}M_{2,3}$ transitions for a 75-Å Ti film as a function of annealing conditions. The Ti and Si AES intensities are measured relative to pure Ti and pure Si, respectively, and the data are plotted in terms of relative Ti concentration in the film (as opposed to Si concentration).

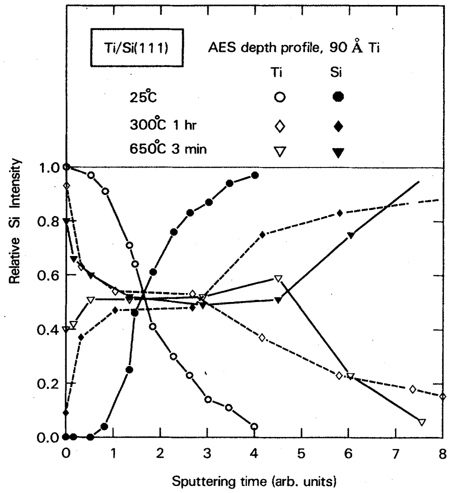

FIG. 6. AES sputter profiles of a 90-Å Ti film at 25 °C, reacted at 300 °C (1 h), and reacted at 650 °C (3 min). The Ti $L_{2,3}M_{2,3}M_{2,3}$ and Si $L_{2,3}VV$ AES intensities are measured relative to pure Ti and pure Si, respectively, and the data are plotted in terms of relative Si intensity.

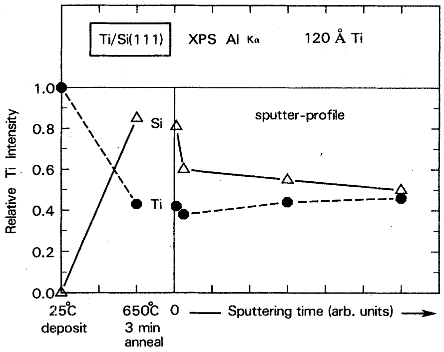

FIG. 7. XPS intensities [from Si($2p$) and Ti($2p$) core levels] for deposition of a 120-Å Ti film at 25 °C, reaction at 650 °C for 3 min, and sputter profiling with XPS into the overlayer. The XPS intensities are depicted relative to pure Ti and pure Si respectively, and the data are plotted in terms of relative Ti concentration in the film (as opposed to Si concentration).

pressed in terms of partial Si concentration in Fig. 6. The data points were taken as a function of sputtering time; the x axis is labeled simply as effective depth in arbitrary units.

The depth profiles for the 25 °C film are initially flat, indicating a pure Ti overlayer. At larger depth the change from pure Ti to pure Si appears gradual as a result of preferential sputtering and ion knock-on effects; these artifacts are well known to occur in ion sputter profiling even for an abrupt interface, with broadening typically ~30 Å in depth. The unreacted Ti/Si interface should be approximately at the midpoint of these compositional transitions, i.e., at ~1.5 units in depth for the 90-Å film.

As shown in Fig. 6, the 650 °C annealing caused substantial reaction and intermixing of Ti and Si across the initial Ti/Si interface. As a result, the profiles for both species are considerably broader than observed for the as-deposited (25 °C) sample. The mixed composition is fairly uniform through the 650 °C reacted layer. Structural studies (by TEM), described below, showed that this layer is $TiSi_2$. The composition indicated in Fig. 6 from Auger sputter-profiling studies appears somewhat different from this (closer to TiSi), but we attribute this difference to preferential sputtering effects due to different sputter yields for Ti versus Si. Finally, the measured composition of the top surface appears more Si rich; this probably reflects preferential Si segregation to the top surface of the silicide (as has been found in cases of other silicides) or that preferential sputtering has not yet shown its effect and a more accurate representation of the $TiSi_2$ composition is achieved.

The results for 300-°C annealing in Fig. 6 also give clear evidence for low-temperature reaction. The profiles are broader than those observed for the unreacted case (25 °C). Although the width of the mixed region is less than that for the 650-°C case, the indicated composition is similar. Furthermore, the intermixed region changes gradually with depth into the Si substrate than for the 650-°C case. This suggests the possibility of nonuniform reaction or incomplete silicide formation, a situation somewhat different that the higher-temperature silicide growth; stronger evidence for this from TEM structural studies will be described below. Finally, the composition of the top surface for 300-°C annealing is more Ti rich, contrary to the 650-°C case, indicating the presence of some unreacted Ti after this annealing step.

Similar results for the depth profile of a high-temperature reacted film are shown from XPS in Fig. 7. Starting from a 120-Å Ti film, the surface composition changes to ~$TiSi_2$ after a 650-°C, 3-min annealing process. Upon sputter profiling into the overlayer, the apparent composition becomes more Ti rich, as expected from the preferential sputtering and seen in the AES profiling results in Fig. 6.

V. STRUCTURAL PROPERTIES OF REACTED Ti-Si OVERLAYERS

The surface spectroscopy measurements discussed above provide information on three aspects of the Ti/Si interfacial chemistry—the composition, the reactivity, and the electronic structure. To properly interpret these results it is important to identify the compound phases formed at the interface and in the reacted overlayer. This has been accomplished using TEM to reveal both the compound phases and microstructure.

With annealing to temperatures ≥500 °C, Ti silicide phases are formed, as expected from previous thin-film studies.[19] This is demonstrated for 650-°C annealing (3-min) of a 200-Å Ti film on clean Si(111) by the TEM results in Fig. 8. The diffraction pattern shows rings which are characteristic of $TiSi_2$, including (313), (004), and (022) together, and (311). No rings for TiSi are evident. At the same time, the bright field micrograph displays the $TiSi_2$ grains, which are ~1000–2000 Å in size. Thus the brief reaction at 650 °C converts the Ti to $TiSi_2$ at this clean interface.

The situation is somewhat more complex for thinner Ti

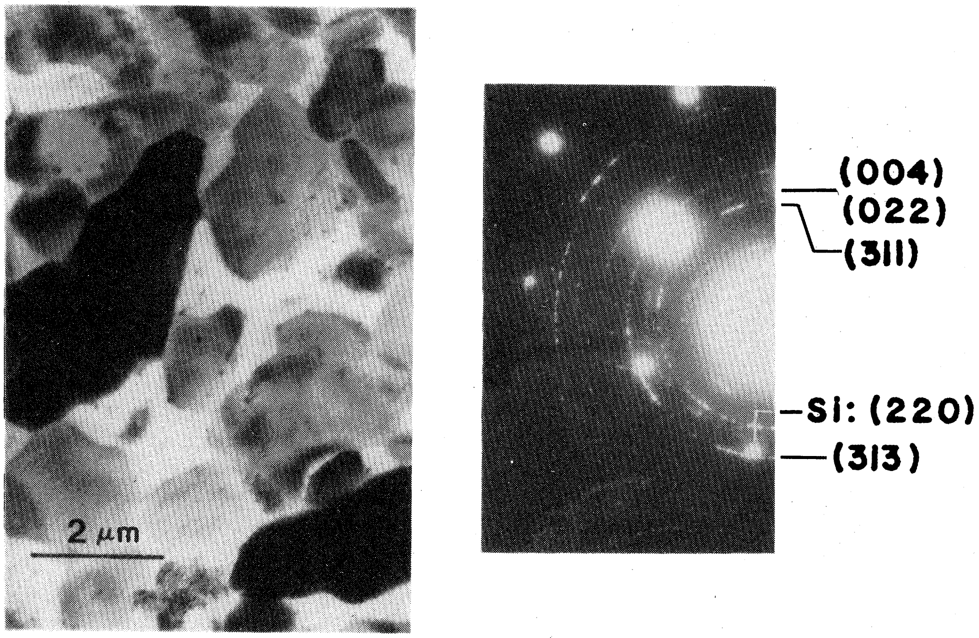

FIG. 8. (a) TEM bright field micrograph of a 200-Å Ti film on atomically clean Si(111) reacted at 650 °C for 3 min; (b) corresponding diffraction pattern indexed for $TiSi_2$.

overlayers and/or lower annealing temperatures, as demonstrated in Fig. 9. Here the diffraction pattern for a 30-Å Ti film reacted at 600 °C for 30 min shows rings characteristic of both $TiSi_2$ and TiSi. The $TiSi_2$ rings are the same ones already noted in Fig. 8 (shown with subscript *b* in Fig. 9), while additional TiSi rings (020), (112), and (102) and (210) together (shown with subscript *a*) are also present. The corresponding bright field micrograph reveals a somewhat different microstructure with a networklike appearance and smaller grain sizes.

The microstructure of the layer reacted at lower temperatures (~300 °C) is very different from that of the silicides formed by high-temperature reaction. This can be seen in Fig. 10, which shows the diffraction pattern and dark field micrograph of a 100-Å Ti film deposited on atomically clean Si(111) and then annealed at 300 °C for 20 min. Here the reaction produces extremely fine grain polycrystalline material, with grain size ~10—30 Å (max-

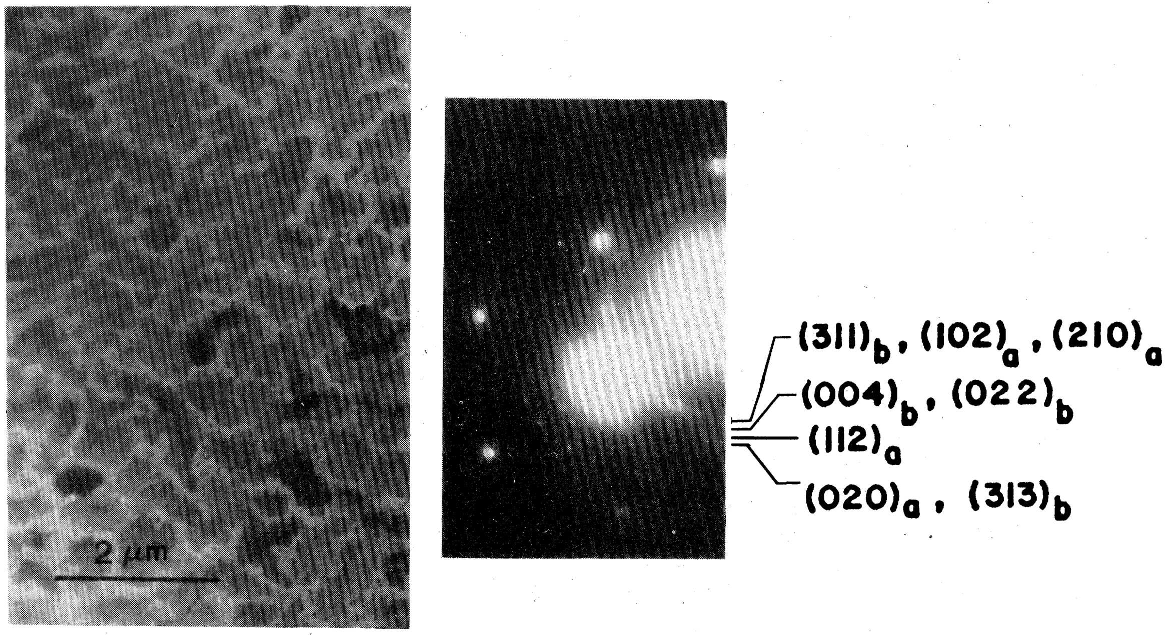

FIG. 9. (a) TEM bright field micrograph of a 30-Å Ti film on atomically clean Si(111) reacted at 600 °C for 30 min; (b) corresponding diffraction pattern indexed for both TiSi (subscript *a*) and $TiSi_2$ (subscript *b*).

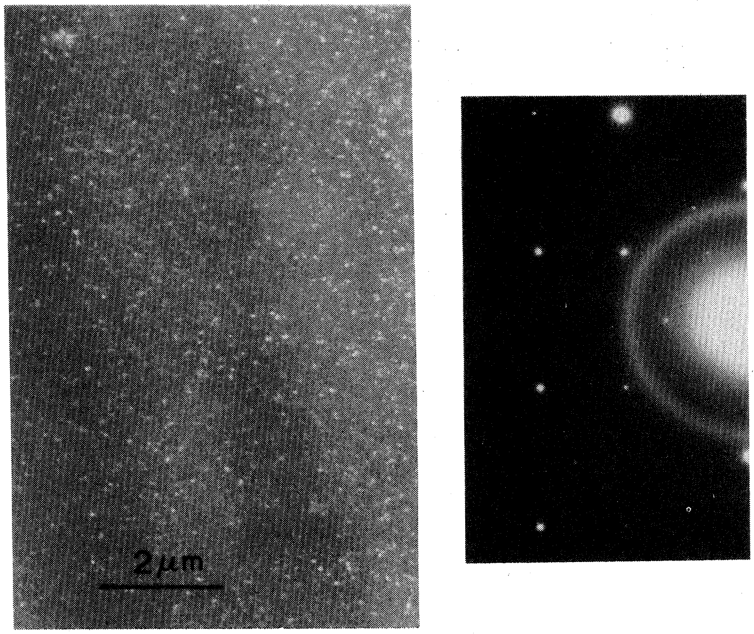

FIG. 10. (a) TEM dark field micrograph of a 100-Å Ti film on atomically clean Si(111) reacted at 300 °C for 20 min; (b) corresponding diffraction pattern.

imum 50 Å). This is manifested also by the diffuse diffraction pattern. A fine-grain $TiSi_2$ structure alone cannot explain all the diffuse rings, so there must be at least two silicide phases present. Upon a subsequent annealing at 780 °C for 3.5 h, part of the overlayer was converted to larger grain (~500—1500 Å) TiSi and $TiSi_2$. However, the very fine grain material still remains in substantial quantity (with a somewhat larger grain size, ~100 Å), even though the temperature and time were considerably more than normally required for complete conversion to $TiSi_2$ (as at 650 °C for 3 min in Fig. 8). Thus reaction at low temperature changes the microstructure of the intermixed layer as well as the kinetics with which the microstructure evolves into larger grain, more typical silicide material.

VI. DISCUSSION OF REACTION PROCESSES

To understand the essential chemical behavior of the Ti/Si interface, it is necessary now to synthesize the information from surface spectroscopy observations of composition and electronic structure with that from TEM studies of the lattice structure and microstructure. This is most readily accomplished by dividing the discussion into three parts: (i) unreacted interface, (ii) silicide formation process at high temperature, and (iii) low-temperature intermixing reaction.

A. Unreacted interface ($T \leq 250\,^{\circ}\mathrm{C}$)

At temperatures below ~250 °C, reaction involving atom motion across the interface is insignificant. This is clear from the composition measurements by AES and XPS in Figs. 1 and 5—7, which are sensitive to atomic mixing over distances ~100 Å. Furthermore, the low coverage results in Fig. 1 (~ monolayer range) also show no atomic mixing across the interface, in contrast to the usual behavior of the near-noble transition metals. Finally, the interface electronic structure at low coverage (~1—15 monolayers), seen in the UPS spectra in Fig. 3, reveal Ti($3d$)-derived bands more similar in shape to those of pure Ti metal than those of bulk $TiSi_2$,[14] again suggesting that the interface remains unreacted. The observation of a fully unreacted state of the interface for temperatures ≤250 °C provides an opportunity to observe the onset of interfacial reaction with thermal processing, which has not been possible for most transition-metal/Si interfaces.[1,2]

B. Silicide formation at high temperature ($T \geq 500\,^{\circ}\mathrm{C}$)

Thin-film investigations[18—22] have previously shown that Ti silicide growth over ~100 Å or more begins at ~500 °C, with initial formation of TiSi and subsequent growth of $TiSi_2$ at higher temperatures (~650 °C). The present measurements demonstrate similar behavior at atomically clean Ti/Si interfaces. The TEM structural studies show that annealing at 650 °C produces the lattice structure of $TiSi_2$ with reasonably large silicide grains (~500—1500 Å), as seen in Fig. 8, while at lower temperature (~600 °C) and/or for thinner Ti overlayers, TiSi is also present (see Fig. 9).

The composition measurements by AES and XPS in Figs. 1, 2, and 4—7 also demonstrate the strong Ti-Si intermixing which must accompany the formation of $TiSi_2$ and TiSi compounds. Composition measurements carried out with a variety of atom-specific AES and XPS lines with different electron escape depths ranging from ~8 Å (e.g., Si $L_{2,3}VV$ in AES) to ~25—30 Å [e.g., Si($2p$) and Ti($3p$) in XPS, Si KLL in AES] indicate a Ti:Si composition ~1:2 for 650 °C reaction with a variety of such escape depths, as seen in Figs. 5—7. This suggests that reaction at 650 °C produces an overlayer composition ~ that of $TiSi_2$ within the top ~25 Å at the surface. In addition, the sputter-profiling data show uniform composition distribution through the reacted layer. Therefore, we conclude that the composition of the reacted layer is approximately $TiSi_2$. Thus the chemical and structural aspects of the high-temperature ($\geq 500\,°C$) reaction at the Ti/Si interface are consistent with the previous observations of silicide compound formation by interfacial (contact) reaction.

C. Low-temperature intermixing ($250\,°C \leq T \leq 500\,°C$)

The new information obtained in the present studies of the intrinsic chemistry of the Ti/Si interface comes in the detailed observation of the interfacial reactions in this intermediate temperature range. The reaction is distinguished not only by the presence of initial silicide formation at temperatures well below those normally used for formation of thin-film silicides, but by markedly different microstructural characteristics of the reacted layer as compared to those produced by silicide growth at higher temperatures, either for atomically clean or more common, chemically cleaned Si surfaces.

Compositional evidence for this low-temperature ($\leq 250\,°C$) intermixing over considerable distances from the initial interface is clear from the AES results in Figs. 1, 2, and 4—6. The AES depth profile in Fig. 6 also demonstrates that Ti and Si are mixed throughout the entire overlayer, with an apparent composition (as seen in Auger sputter profiling) which is similar to that obtained by high-temperature reaction.

From the surface spectroscopy measurements, the temperature and time dependence of the intermixing reaction seen in Fig. 5 seems uncharacteristic of the simple silicide compound formation process. For typical activation energies of refractory silicide formation, one would expect a much more rapid transformation of the composition of the overlayer surface from pure Ti to the Ti-Si mixture than is observed. Such a rapid transformation has been seen in annealing studies of ≥ 50 Å near-noble transition metals on Si in several cases.[1,2,26]

The microstructural information from TEM studies clarifies the different nature of the Ti-Si interfacial reaction at low temperatures ($250\,°C \leq T \leq 500\,°C$) compared with that at high temperatures ($T \geq 500\,°C$). As shown in Fig. 10, the 300-°C-reacted material is polycrystalline with very fine grain size of order 10—30 Å, which may represent nonuniform reaction. This is very different from the microstructure of well-defined $TiSi_2$ layers formed by reaction at higher temperatures (see Figs. 8 and 9).

This intermediate reaction can alter significantly the structure and phase kinetics for subsequent high-temperature annealing, as demonstrated by two observations. First, a fraction of the very fine grains persist even at high temperatures. Second, once this stage has proceeded throughout the overlayer, the kinetics of forming the expected silicide material with larger grains and well-defined lattice structure is considerably altered: Even though 650 °C for 3 min was sufficient without prior low-temperature intermixing (see Fig. 8), annealing at notably higher temperature (780 °C) for a longer time (3.5 h) does not completely convert the low-temperature reacted material to more conventional silicide (see Fig. 11). Thus the low-temperature reactivity of the Ti/Si interface presents considerably complexity, which may involve difficult issues of the interrelation between nucleation phenomena, phase stability, and thin-film silicide formation at interfaces.[27,28]

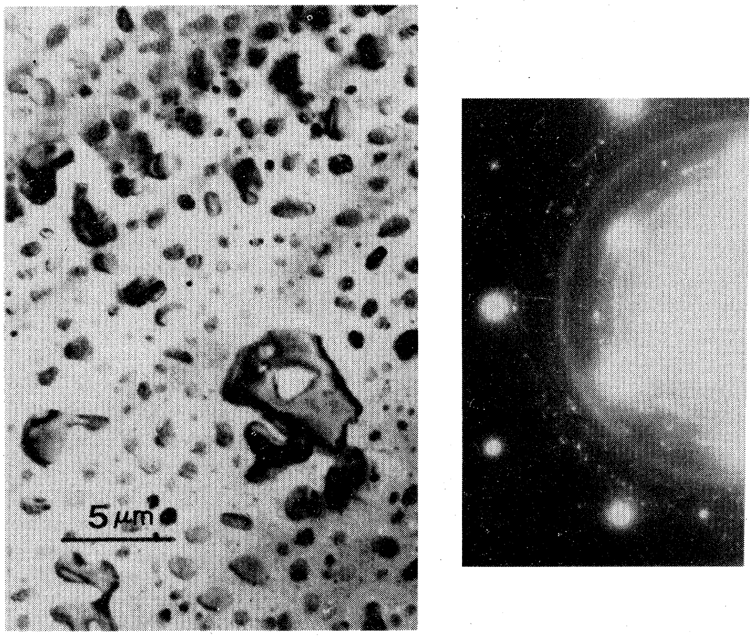

FIG. 11. (a) TEM bright field micrograph of a 100-Å Ti film on atomically clean Si(111) reacted at 300 °C for 20 min and then at 780 °C for 3.5 h; (b) corresponding diffraction pattern.

VII. CONCLUSIONS

The main conclusions of this work can be summarized as follows.

(1) Below $\sim 250\,^{\circ}\mathrm{C}$ the Ti/Si interface remains *unreacted,* i.e., no significant motion of Ti or Si atoms across the interface occurs. In contrast to most transition-metal/Si interfaces, the initial stage of silicide compound formation (establishment of a few unit cells of silicide at the metal/Si interface) does not proceed spontaneously to any significant extent at the Ti/Si interface, even when atomically clean.

(2) For temperatures above $\sim 500\,^{\circ}\mathrm{C}$, the dominant interfacial reaction process is that of silicide compound formation, which leads to the formation of primarily polycrystalline TiSi_2, with a trace amount of TiSi. These silicide layers are composed of grains $\sim$500—1500 Å in size.

(3) Interfacial reaction begins at $\sim 250\,^{\circ}\mathrm{C}$, i.e., well below normal silicide formation temperatures. The reaction in the intermediate temperature range of $\sim 300\,^{\circ}\mathrm{C}$ involves initial, probably nonuniform formation of silicides with very fine grains and Ti-Si intermixing over a considerable distance ($\sim$100 Å or more) from the initial interface. In these situations the overlayer composition is close to that of TiSi_2.

(4) Following thorough intermixing at low temperature, subsequent annealing at high temperatures does not completely convert the complete overlayer into the expected form of silicide. Thus this intermediate reaction stage can markedly change the kinetics and structure for subsequent high-temperature formation of silicides.

These results give new information about the essential chemical behavior of the Ti/Si interface. The role of low-temperature intermixing is particularly striking since it can alter significantly the kinetic path and structure of silicide compound formation. To what extent this is affected by the use of an atomically clean interface is not yet clear. Further work is needed to elucidate the microscopic behavior of the refractory transition-metal/Si interface, so that a meaningful picture of chemical trends throughout the transition-metal series can be developed and a better understanding of the essential steps in the interfacial reactions can be achieved.

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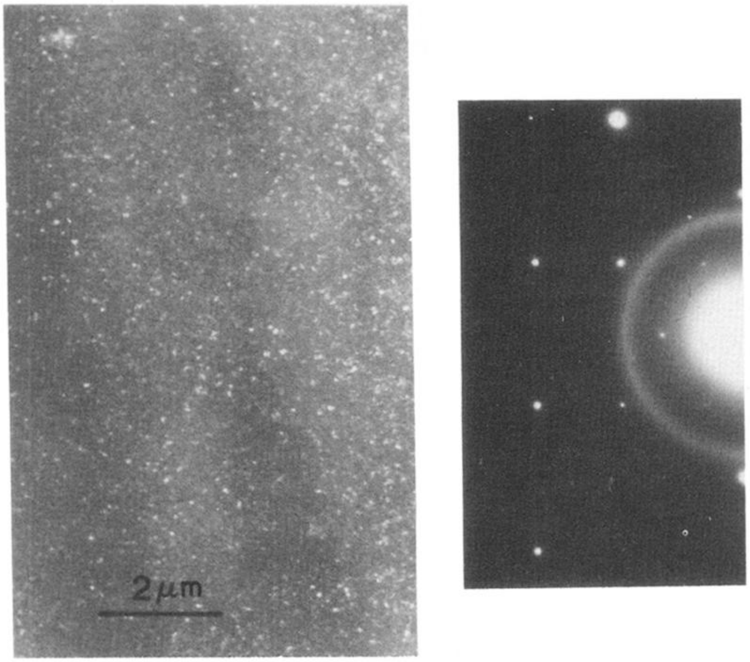

FIG. 10. (a) TEM dark field micrograph of a 100-Å Ti film on atomically clean Si(111) reacted at 300 °C for 20 min; (b) corresponding diffraction pattern.

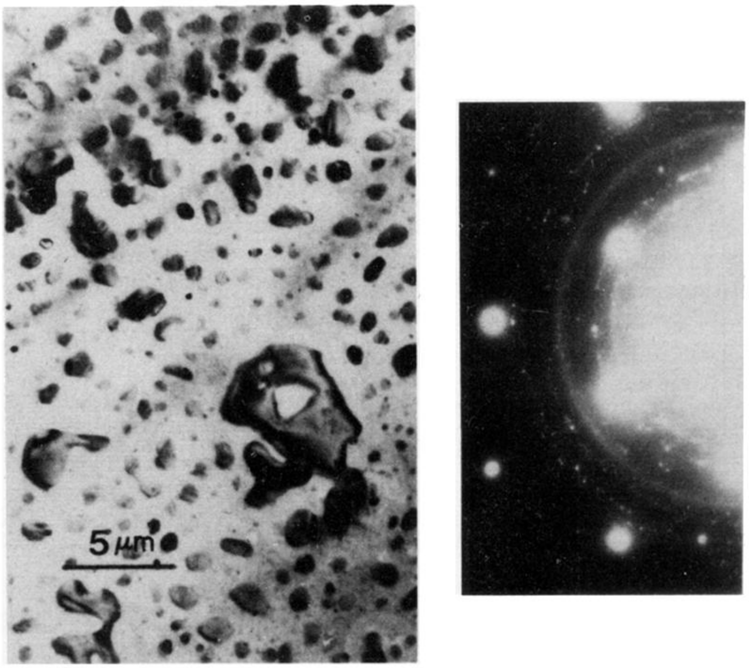

FIG. 11. (a) TEM bright field micrograph of a 100-Å Ti film on atomically clean Si(111) reacted at 300 °C for 20 min and then at 780 °C for 3.5 h; (b) corresponding diffraction pattern.

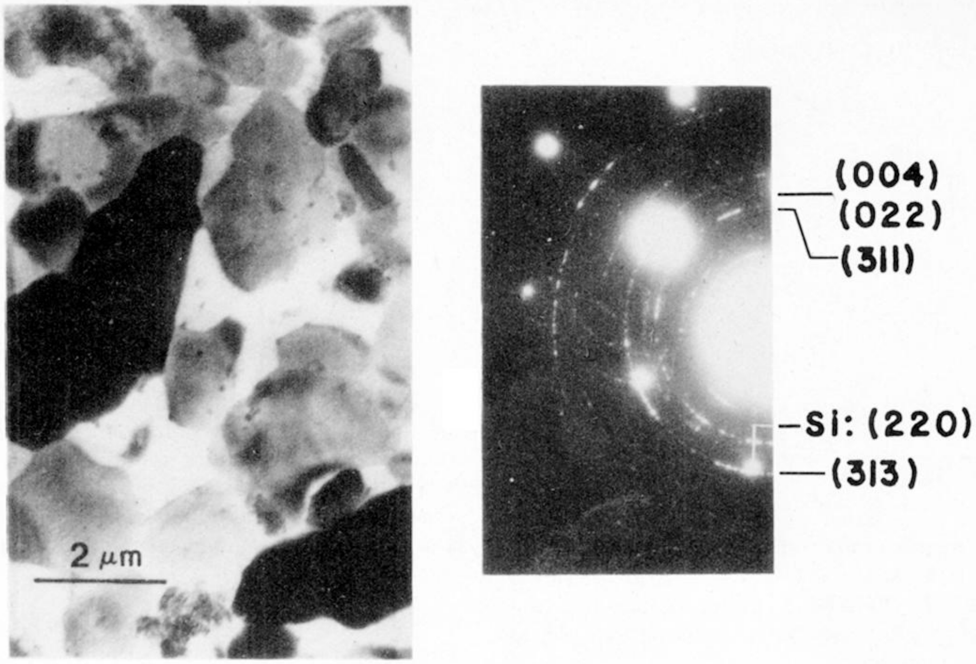

FIG. 8. (a) TEM bright field micrograph of a 200-Å Ti film on atomically clean Si(111) reacted at 650 °C for 3 min; (b) corresponding diffraction pattern indexed for $TiSi_2$.

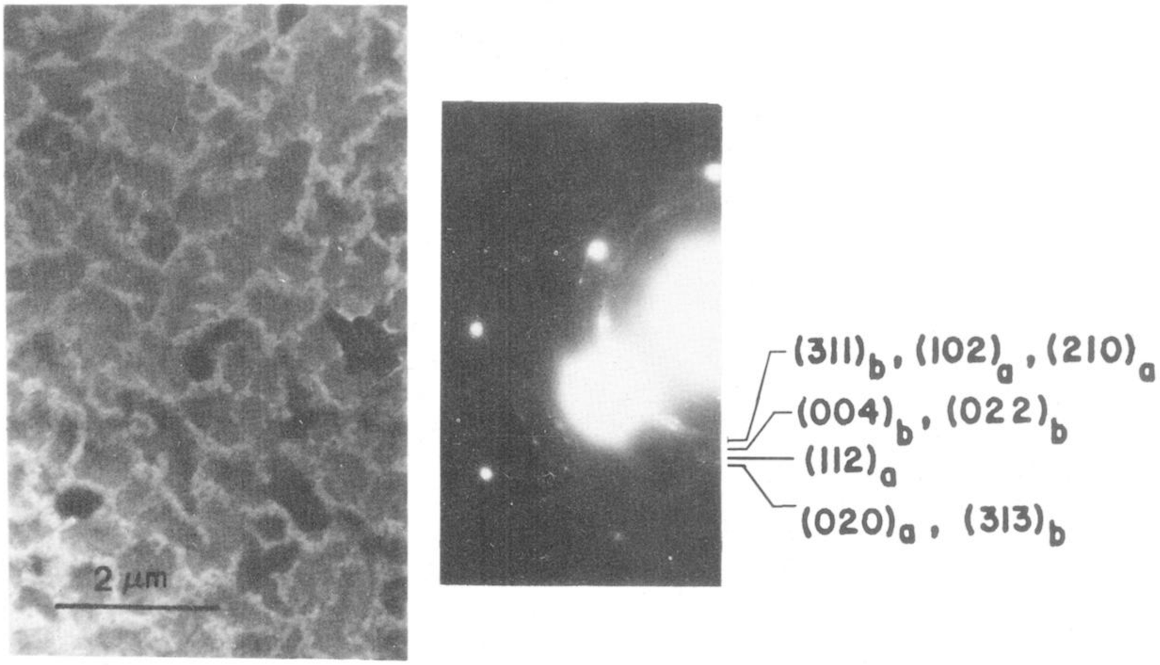

FIG. 9. (a) TEM bright field micrograph of a 30-Å Ti film on atomically clean Si(111) reacted at 600 °C for 30 min; (b) corresponding diffraction pattern indexed for both TiSi (subscript *a*) and $TiSi_2$ (subscript *b*).