Initial growth of Ti on Si

J. Vähäkangas

Institute of Technical Physics, University of Oulu, SF-90570 Oulu 57, Finland

Y. U. Idzerda, E. D. Williams, and R. L. Park

Department of Physics and Astronomy, University of Maryland, College Park, Maryland 20742

(Received 11 February 1986)

The structural and electronic properties of low coverages of Ti deposited on Si(100) and Si(111) at room temperature have been investigated by detailed Auger-electron spectroscopy, low-energy electron diffraction (LEED), and appearance-potential spectroscopy (APS). The growth mechanism is dependent on the cleaning procedure. When the sample is cleaned by brief thermal annealing at 850 °C alone, Ti growth is layer-by-layer on both Si(100) and Si(111). When cleaned by sputtering and heating, the Ti growth on both surfaces is characteristic of island growth following a Poisson distribution. The Si(111) (7×7) and (1×1) LEED beams are extinguished by deposition of less than a monolayer of Ti, as are the Si(100) (2×1) and (1×1) beams. This indicates a marked disruption of the Si lattice in the near surface region due to Ti. Appearance-potential spectra show development of structure characteristic of the pure Ti surface beginning at coverages of less than a monolayer. The growth mode and the APS results are inconsistent with intermixing of the Ti and Si on either Si(111) or Si(100) at room temperature.

I. INTRODUCTION

The recent focus of a growing fraction of metal-silicon interaction studies, a subject which has long been of great interest to the semiconductor community,^{1,2} has been the refractory transition-metal-silicon systems.³⁻¹⁶ These silicide/Si systems have a number of interesting properties including low-resistance,³ well-defined, and controllable interfaces,⁴ low barrier contacts,^{5,6} strong adhesion,^{7,8} and possibilities for passivation.⁹⁻¹¹ A detailed understanding of these properties requires a better understanding of the interface chemistry, specifically Si–Si bond breaking which is a necessary prerequisite to silicide formation.

Studies on the growth of titanium on clean silicon surfaces have led to controversial results as to the reactivity of the interface at room temperature. Based on Augerelectron spectroscopy (AES) and ultraviolet photoemission spectroscopy (UPS) measurements, Butz et al.¹² conclude that the Ti-Si(111) interface remains unreacted at room temperature. Taubenblatt and Helms⁵ came by UPS to the same conclusion on the Ti-Si(100) system. On the other hand, results of a recent ion backscattering study by van Loenen et al.¹³ have been interpreted as due to intermixing at the Ti-Si(111) interface at room temperature. Similar observations were made by Iwami et al.¹⁴ by electron-energy-loss spectroscopy (EELS), but only for Ti overlayer thicknesses greater than about 2.5 monolayers (ML), the so-called critical thickness, and by Franciosi and Weaver¹⁵ in photoemission work. Very little attention has been paid to the growth mode of Ti on Si surfaces, as well as to atomic and electronic structures of very thin Ti films on Si surfaces, subjects of direct bearing on interface chemistry and reactivity.

on the growth mode of Ti on atomically clean Si(100) and Si(111) surfaces using AES, low-energy electron diffraction (LEED), and appearance-potential spectroscopy (APS). We find that the initial growth of the Ti on the Si surface is delicately dependent upon the surface cleaning procedure. Here we are able to show that on heat-cleaned Si surfaces, Ti grows in a layer-by-layer fashion, whereas on sputter-cleaned Si surfaces the growth mode changes to island formation. Upon closer examination, the physical mechanism underlying the island formation appears to be an inhibition of surface diffusion of the randomly deposited titanium, resulting in a statistical distribution of overlayer thickness.

Layer-by-layer formation of the Ti is taken to indicate a strong substrate-adsorbate interaction. The strength of the Ti-Si interaction is further demonstrated by the complete loss of long range surface order upon deposition of less than the equivalent of one layer of Ti. The details of the long-range order disruption are not yet clear, but once understood, they should shed light on the Si-Si bondbreaking mechanism.

The structural results however do not indicate any intermixing of the silicon and titanium. Intermixing beyond the first layer is not consistent with the observation of layer-by-layer growth. Furthermore, measurements of the electronic properties via APS do not support the possibility of intermixing. The appearance potential spectrum for a pure Ti layer includes a surface state, present as a shoulder on the edge of the 2p levels. This shoulder disappears when the Ti atoms form a chemical bond with a different species. For Ti deposited on Si at room temperature, this shoulder is apparent even at small coverages indicating that the intermixing of the Ti with the substrate to form a silicide does not occur.

In this study, our goal is to obtain detailed information

33 8716

II. EXPERIMENTAL TECHNIQUES

The experiments were conducted in an ion and Tisublimation-pumped ultrahigh vacuum (UHV) system with a base pressure $< 2 \times 10^{-10}$ Torr. The system is equipped with LEED/Auger-electron optics with coaxial electron gun, a single-pass cylindrical mirror analyzer (CMA) with coaxial electron gun which was used for AES, a quadrupole mass spectrometer, a quartz-crystal microbalance (QCMB), and an Ar^+ ion sputtering source. The silicon samples were boron doped, p-type wafers $(35-50 \ \Omega \text{ cm}, 0.4 \text{ mm thick})$ with (100) and (111) orientations. The samples were approximately 1×1 cm² in area and were thermally anchored to a resistive sample heater by a molybdenum clamp and a very small amount of indium inserted between the surface of the heater and the back side of the silicon. A carousel sample holder allowed for multiple sample installation in the UHV chamber (up to four independently heated samples). Temperatures were measured by optical pyrometry.

Samples were cleaned by two different methods. In the first, the Si samples were cleaned by annealing at ≥ 850 °C for several minutes to remove the oxide layer. As a result, sharp Si(111)-(7 \times 7) and Si(100)-(2 \times 1) LEED structures were obtained. AES showed only traces (<1%) of contaminants (mainly carbon). Excessive or extended heating led to increased carbon contamination presumably due to segregation from the Si bulk to the surface. In the second cleaning technique, the surface was heated briefly at 850 °C, then sputtered lightly ($I_{Ar} = 20 \ \mu A$, $E_{Ar} = 900 \ eV$) for 20 min at room temperature. The sample was then annealed at 850°C for 10 min to restore surface order. This results in the same LEED and AES characteristics as heat cleaning alone. For both cleaning procedures, LEED and AES results indicate no indium segregation from the backside to the Si surface. Indium contamination is expected to result in the lessening of the fourth-order bright spots in the Si(111)-(7 \times 7) LEED pattern. Higher indium contamination results in a $\sqrt{3} \times \sqrt{3}$ overlayer LEED pattern.¹⁷ Examination of the Si/indium-heater junction showed localized alloying at the center of the back of the silicon. These results suggest that, for sufficiently small amounts of indium, the indium remains trapped at the junction.

The Ti films were evaporated onto the Si substrate from a thoroughly outgassed, directly heated Ti-Ta alloy wire. Typical deposition rates were $\frac{1}{3}$ of a monolayer per minute, though uniform deposition rates as low as $\frac{1}{6}$ of a layer per minute and as high as 3 layers per minute were routinely achieved. The Ti deposition rate was measured by a QCMB to be constant over extended periods (equivalent to > 30 layers) but did slowly decrease as the source exhausted its Ti supply. The amount of Ti deposited on the substrate was determined from the measured deposition times. After all depositions, AES again showed only traces of contaminants, and no Ta signal was present in the AES spectra. During deposition, the background pressure remained below 5×10^{-10} Torr.

The appearance potential spectra were taken by the disappearance-potential spectroscopy (DAPS) technique, $^{18-20}$ using the LEED optics to measure the quasi-

elastic scattering yield as the energy of the electrons incident on the sample is swept through the Ti 2p excitation thresholds. Only those electrons that had lost less than 10 eV of energy from the incident electron energy (quasielastically scattered electrons) were detected. To enhance the small, rapidly fluctuating DAPS spectrum, the first derivative of the quasielastic yield was measured by applying a 0.2-V peak-to-peak modulation voltage to the sample potential and using lock-in detection techniques.

III. Ti OVERLAYER GROWTH MODE

In Figs. 1 and 2 we show the first derivative Auger intensities of the Si $L_{2,3}VV$ (90 eV) and Ti $L_{3}M_{2,3}M_{2,3}$ doublet (385 eV) transitions for the Si(100) and Si(111) surfaces, respectively, as a function of Ti deposition. These results are for surfaces cleaned by heating alone. On both Si surfaces, the AES intensity versus Ti deposition can be separated into linear sections which display sudden changes in slope at equal deposition intervals and at corresponding depositions for the Si and Ti signals. This behavior of the Auger intensity is indicative of a layer-by-layer (Frank-van der Merwe) growth,^{21,22} where the sudden changes in slope, or breaks, in the AES versus deposition are taken to indicate completion of another monolayer in the growth of the overlayer. Using the break points as indicators of monolayer completion, we can calibrate the number of atoms in a monolayer of the Ti overlayer. We find that QCMB measurements indicate that for both silicon surfaces, one layer is $1.5\pm0.2\times10^{15}$ atoms/cm², near the expected value of 1.3×10^{15} $atoms/cm^2$ for the Ti(0001) surface.

A linear regression through the interior points between the breaks of the Si $L_{2,3}VV$ signal gives straight lines with a goodness of fit, $r^2 \ge 0.98$. This is significantly better than a fit of the data to an exponential function, which gives a goodness of fit $r^2 \sim 0.90$. The extrapolated value of the first linear segment back to zero Ti deposition is used for the initial substrate intensity I_0 . In Figs. 1 and 2, the substrate plots have been normalized so that $I_0 = 100\%$. Since the intersection of the straight lines signifies the completion of succeeding layers of Ti, the Auger-intensity measurements at these intersections are for full fractional coverages. At these points, the Auger intensity is just

$$I_{\rm sub}(t) = I_0 \exp\left[-t/l\cos(42^\circ)\right],$$

where t is the full fractional coverage thickness (an integer number of layers), l is the decay length, and the factor of $\cos(42^\circ)$ results from the entrance angle of the CMA.²³ Least-squares fitting our few points to this function results in a very good fit with values for l of 1.8 and 1.6 monolayers for the Si(100) and Si(111) surface, respectively. Using the value of 2.34 Å for the interlayer spacing of Ti, results in an inelastic mean free path (IMFP) of 4.1 ± 0.3 Å and 3.9 ± 0.3 Å for the Si *LVV* Auger electrons of the Si(100) and Si(111) surface, respectively.²⁴ This is in good agreement with the value of 4.2 Å found in the literature,²⁵ but in disagreement with the value of 8–9 Å as measured by others.^{12,26,27} This apparent discrepancy will be discussed later.



FIG. 1. First-derivative-normalized Auger intensities of the Si (\odot) $L_{2,3}VV$ (90 eV) and Ti (\odot) $L_3M_{2,3}M_{2,3}$ doublet (385 eV) as a function of Ti deposition on the Si(100) surface. Least-squares straight-line fits to segments of the data points are shown (---). This behavior is indicative of layer-by-layer growth. We can establish values for the inelastic mean free path (see text) of 4.1 ± 0.3 Å for the (90 eV) Si Auger electrons, and 5.7 ± 0.3 Å for the (385 eV) Ti Auger electrons.



FIG. 2. First-derivative-normalized Auger intensities of the Si (\odot) $L_{2,3}VV$ (90 eV) and Ti (\odot) $L_3M_{2,3}M_{2,3}$ doublet (385 eV) as a function of Ti deposition on the Si(111) surface. Least-squares straight-line fits to segments of the data points are shown (---). This behavior is indicative of layer-by-layer growth. We can establish values for the inelastic mean free path (see text) of 3.9 ± 0.3 Å for the (90 eV) Si Auger electrons, and 5.7 ± 0.3 Å for the (385 eV) Ti Auger electrons.

The Auger signal from the Ti overlayer shows similar linear sections for both surfaces, even though the breaks are not as pronounced as for the substrate signal. Again, the extrapolated intersection points of these straight line segments signifies completion of another layer of the Ti overlayer and can be fit to the relation

$$I_{ads}(t) = I_{\infty} \{1 - \exp[-t/l\cos(42^{\circ})]\}$$

where both the high coverage Auger intensity I_{∞} and the decay length l are parameters of the fit. The high coverage values determined from our fits and used to normalize the adsorbate plots of Figs. 1 and 2 (so that $I_{\infty} = 100\%$) are slightly higher than the measured high coverage Auger intensities. The value for the decay length as determined by this fit is 2.4 ± 0.1 monolayers for both surfaces, in excellent agreement with other values of 2.45 ± 0.05 layers for Ti on W,²² and associated with a reasonable²³ IMFP of 5.7 ± 0.3 Å for the 385-eV electrons.

The results above are not consistent with intermixing at the interface (excluding perhaps the growth of the first layer). If there were intermixing in succeeding layers, the Si signal would decay more slowly than observed. Moreover, the layer-by-layer growth observed would be difficult to interpret in terms of intermixing. Additional evidence for nonintermixing of the Ti overlayer is found in the absence of the slight shift of the Si $L_{2,3}VV$ Auger line shape (characteristic of titanium silicide^{28,29}) as Ti is deposited on the clean Si. At higher coverages (>4 layers) the Auger signals associated with the interface are very small due to the short IMFP, and our measurements show no Si in the probed region.

If we use a different, though common,^{12,13,16,26} surface cleaning procedure involving sputtering as well as heating, the overlayer growth characteristics become quite different. The first derivative Auger intensities of the Si $L_{2,3}VV$ (90 eV) and Ti $L_3M_{2,3}M_{2,3}$ doublet (385 eV) transitions as a function of Ti deposition for the sputtercleaned Si(100) surface are shown in Fig. 3. Very similar results are obtained for the Si(111) surface. Two aspects are immediately apparent: first, the much more gradual change in Auger intensities (at a Ti deposition time equivalent to a uniform coverage of 3 layers, the Si Auger intensity is still at $\sim 20\%$ instead of 8% as in Figs. 1 and 2); and second, the absence of linear segments separated by abrupt changes in slope. This AES behavior can be explained in terms of island growth or of limited intermixing. The possibility of intermixing, however, is ruled out on the basis of the surface electronic properties as discussed in Sec. V.

The physical mechanism responsible for the island formation observed here is suggested to be statistical in nature. The variations in the overlayer thickness are created by random Ti deposition associated with strongly hindered surface diffusion of Ti. This resulting statistical distribution in overlayer thickness (a Poisson distribution) was forwarded by van Loenen *et al.* as an explanation for ion backscattering measurements performed on Ticovered Si(111) surfaces cleaned by sputtering and annealing.^{13,16} For a Poisson distribution in overlayer thickness, we can calculate the Auger intensities of the Si substrate and the Ti overlayer from



FIG. 3. First-derivative-normalized Auger intensities of the Si (\oplus) $L_{2,3}VV$ (90 eV) and Ti (\bigcirc) $L_{3}M_{2,3}M_{2,3}$ doublet (385 eV) as a function of Ti deposition on an Ar⁺ sputtered and annealed Si(100) surface, on a roughened Si(100) surface (\blacksquare), and on an Ar⁺ sputtered and annealed Si(111) surface (\blacktriangle) from Butz et al. (Ref. 12). Also shown in the solid line ($__$) are the calculated values for a CMA-measured Auger intensity for a Poisson distribution of overlayer thickness using measured values for the IMFP as determined from layer-by-layer AES data.

substrate:
$$\frac{I}{I_0} = \sum_{n=0}^{\infty} P(n,\mu) \exp\left[\frac{-n\tau}{l\cos(42^\circ)}\right];$$

adsorbate: $\frac{I}{I_{\infty}} = \sum_{n=0}^{\infty} Q(n,\mu) \exp\left[\frac{-n\tau}{l\cos(42^\circ)}\right],$

where $P(n,\mu)$ is the fraction of the surface covered with *n* layers, $Q(n,\mu)$ is the fraction of the surface covered by more than *n* layers, μ is the average number of layers in the overlayer, τ is the thickness of one layer, and *l* is the IMFP. For a Poisson distribution,

$$P(n,\mu) = \frac{\mu^n}{n!} e^{-\mu}$$

and

$$Q(n,\mu) = P(n+1,\mu) + P(n+2,\mu) + P(n+3,\mu) + \cdots$$

= 1-[P(0,\mu)+P(1,\mu) + \cdots + P(n,\mu)].

Using the values obtained from the layer-by-layer growth data for the IMFP, we completely specify the Auger intensity as a function of the amount of Ti deposited. Figure 3 shows these calculated curves overlaying the data for the Si(100) Ar^+ sputtered and annealed surface. The agreement is excellent. Least-squares fitting this data to the Poisson distribution using *l* as the fitting parameter results in an IMFP of 3.9 Å for the Si data and 5.8 Å for the Ti data, differing from the value determined from the layer-by-layer growth by < 5%, well within the uncertainties.

Also shown in Figure 3 are the Ti *LMM* Auger intensity versus Ti deposition for a Si(100) surface roughened by multicycles of Ti deposition and desorption, and the Si *LVV* AES intensity for Ar^+ sputtered and annealed Si(111) taken from Butz *et al.*¹² For the Si(100) roughened surface, the surface showed a marked loss of luster before Ti deposition, consistent with macroscopic surface roughness. It is reasonable to expect limited surface diffusion (Poisson distribution) for heavily damaged (rough) surfaces. The similarity in results for Ti growth on a roughened surface and for the Ar^+ sputtered and annealed surface lends added support to our conclusions of a Poisson distribution of overlayer thickness for the Ar^+ sputtered and annealed surface.

The Si AES data for the sputtered and annealed Si(100) surface is consistent with a Poisson distribution using the value of 4.2 Å obtained earlier for the IMFP. A simple exponential fit to this data (which assumes uniform thickness) results in an apparent value of 8 Å for the IMFP, the same as that obtained by Butz *et al.* for a Si(111) surface. This method for determining the IMFP, though giving useful qualitative results, is semiquantitative, leading to the apparent discrepancy in values for the IMFP. A similar value for the Si *LVV* Auger electrons of 8 Å was determined for *V* overlayers on a sputter-cleaned and annealed Si surface,²⁷ indicating island formation may occur for *V* overlayers.

IV. STRUCTURAL PROPERTIES

LEED measurements were made on Si(100) and Si(111) samples which had been cleaned by heating at 850°C in UHV (no Ar⁺ sputtering). As already mentioned, this resulted in Si(100)-(2×1) and Si(111)-(7×7) LEED structures. When Ti was deposited on these surfaces, the two samples behaved similarly. On Si(111), the seventh-order spots disappeared after only $\sim \frac{1}{5}$ of a monolayer of Ti had been deposited on the surface suggesting that the surface reconstruction was lost. No ordered Ti adsorbate structures were witnessed at these fractional coverageseven with annealing of the overlayer at various temperatures up to 850°C, where the Ti left the surface region. With increasing Ti coverage, the background intensity increased, and the Si(1×1) structure remained sharp up to $\frac{3}{4}$ of a monolayer, after which the (1×1) pattern disappeared. The Ti overlayers showed no ordered LEED pattern below ~ 10 ML, indicating poor order of the overlayer atoms. The Si(100) surface conserved its (2×1) reconstruction upon Ti deposition until $\frac{1}{2}$ of a monolayer of Ti was deposited. The (1×1) structure remained sharp until $\frac{3}{4}$ of a monolayer, after which only a bright background intensity remained. Again, no ordered Ti adsorbate structure was discernable at these low coverages.

The destruction of the LEED structures with single

monolayer Ti coverages indicates extensive long-range order disruption due to Ti adatoms. This disorder must extend well below the top layer to result in complete loss of the LEED structure. LEED measurements on Si surfaces which were lightly Ar^+ sputtered (after the initial 850 °C heat treatment), then annealed at 850 °C for 10 min, resulted in similar behavior, though at slightly higher Ti coverages.

V. ELECTRONIC PROPERTIES

After determining the Ti overlayer growth mode and structural properties, it is informative to monitor the electronic properties of the Ti overlayer. The Ti 2p appearance potential spectrum was scanned repeatedly as Ti was deposited on clean Si(100) and Si(111) surfaces, as shown in Figs. 4 and 5, respectively. (The data includes corrections for the emitter work function.) The region of the spectrum scanned shows both the $2p_{3/2}$ (at 458 eV) and $2p_{1/2}$ (at 464 eV) excitation edges. Features in the $2p_{3/2}$ spectrum are somewhat better resolved than in the $2p_{3/2}$ spectrum because of the longer lifetime of the $2p_{3/2}$ hole.³⁰ Two major observations can be made. First, the



FIG. 4. Series of normalized first-derivative DAPS spectra of the 2p levels for a smooth Si(100) surface at Ti depositions of (a) $\frac{1}{3}$ monolayer, (b) 1 monolayer, (c) > 10 layers, and (d) pure single-crystal Ti(0001). As Ti coverage increases, the surface-state peak shifts, broadens, and splits into a peak and a should-er.



FIG. 5. Series of normalized first-derivative DAPS spectra of the 2p levels for a smooth Si(111) surface at Ti depositions of (a) $\frac{1}{3}$ monolayer, (b) 1 monolayer, (c) 5 layers, (d) > 15 layers, and (e) pure single-crystal Ti(0001).

occurrence of a continuous shift of the $2p_{3/2}$ spectrum maximum by $\sim 1 \text{ eV}$ to higher energy with increasing Ti coverage. Second, the broadening of the spectrum and the appearance of a shoulder on the low-energy side. On both silicon surfaces, this shoulder exists even at submonolayer coverage. In UPS studies,^{5,12} it has been shown that there is no Fermi-level shift associated with the deposition of Ti on Si(100) or Si(111) surfaces. Thus the shift observed here describes a real change in the local density of states (LDOS) above the Fermi level. Layer-by-layer calculations of the electronic structure of a free-standing Ti(0001) film by Feibelman et al.³¹ indicate that although the Fermi level nearly corresponds to a local minimum in the bulk density of states, a strong band of surface states exists at the Fermi level. This surface state is visible as a peak in the single-crystal Ti(0001) spectrum (at 456 and 463 eV), but is merely a shoulder in the Ti on Si spectra where the crystallinity of the Ti overlayer has not yet been established. The presence of a shoulder instead of a welldeveloped peak is also characteristic for polycrystalline pure Ti films.¹⁸ There is a total absence of a shoulder for

TiSi₂ overlayers or Si rich Ti overlayers,²⁸ but this may be due to segregation of the Si to the surface positions for these overlayers. At submonolayer coverages of Ti on Si. the DAPS spectrum agrees quite well with the prediction of the LDOS calculation for a one-monolayer freestanding Ti(0001) layer. By the completion of the first layer, the state visible at lower coverages broadens and we begin to see the "bulk" LDOS behavior in the Ti DAPS spectrum. Very similar results were found for Ar⁺ sputtered and annealed Si(100) and Si(111) surfaces. The occurrence of these spectral features characteristic of pure Ti is further evidence for a lack of intermixing of Ti and Si. This result, and the similarity of the heat-cleaned and sputter-cleaned surfaces confirms that the growth mode on the sputter-cleaned surface is island formation rather than intermixing.

The surface nature of the shoulder at 456 eV is easily demonstrated by altering the probing depth of the DAPS technique by changing the lower limit of the quasielastic scattering yield.¹⁸ Figure 6 shows that as we go from the purely disappearance technique of elastic scattering $(E_{\text{max loss}} = 0 \text{ eV})$ to more quasielastic scattering $(E_{\text{max loss}} = 10 \text{ or } 25 \text{ eV})$, the shoulder becomes less pronounced as the probing depth of the DAPS technique increases. Further verification of the surface dependence of

this feature is established by noting that Ti surface contamination (either $oxygen^{18}$ or $silicon^{28}$) destroys this feature.

We have earlier observed a band of surface states for submonolayer quantities of Ti on Cu(111),³² which was an unexpected result. The behavior of the DAPS spectrum is very similar for Ti on Si, as evidenced in Fig. 7 where a comparison is made for one monolayer coverages of Ti on Cu(111), Si(111), and Si(100). Also shown is a single-crystal Ti(0001) spectrum.

VI. Ti/Si INTERMIXING

Our conclusion that there is no intermixing of Ti and Si beyond the first monolayer at room temperature is in disagreement with the results of van Loenen *et al.*¹³ Using medium-energy ion scattering, they conclude that the first 3–4 Ti layers intermix with the sputter-cleaned Si(111) surface atoms to form a layer with the composition of TiSi. Additional deposited Ti sits atop this layer. The conclusion of intermixing is mainly drawn from backscattering results obtained using the shadowing and blocking technique.¹⁶ In this technique, the He⁺ ion source and detector were aligned with the [$\overline{1}$ 11] and [001] directions, respectively, and the (110) plane was chosen as



FIG. 6. Series of normalized first-derivative DAPS spectra of the 2p levels for 10 layers of Ti deposited on a smooth Si(100) surface as the maximum energy loss of the reflected electrons is increased (increasing the probing depth). The shoulder becomes less pronounced as the maximum energy loss increases from 0 to 25 V (decreasing the surface sensitivity).



FIG. 7. Series of normalized first-derivative DAPS spectra of the 2p levels for one monolayer of Ti on (a) Cu(111), (b) Si(111), and (c) Si(100). Also shown (d) is the normalized first-derivative DAPS spectrum for pure single-crystal Ti(0001).

the scattering plane so that the number of Si atoms visible to the ion source and detector are minimized. In this geometry, a displacement of Si atoms from their lattice sites will result in an increase in the number of Si atoms visible in the surface region. The backscattering results showed that as the amount of Ti deposited on the Ar⁺ sputtered and annealed Si(111) surface increased from 0 to 2.8×10^{15} Ti atoms/cm², the corrected integrated Si peak area increased suggesting that Si atoms were displaced from their lattice positions. Simultaneous with the growth of the Si peak, the high-energy onset of the Si peak remained fixed. This meant that there are areas on the surface where the Si is not covered by the Ti. These combined results were interpreted to represent intermixing at the Ti/Si interface, where more Si atoms are made visible to the ion beam and detector, and some Si is at the surface. Additional Ti deposition beyond 2.8×10^{15} atoms/cm² resulted in no increase in Si peak area and a shift in onset of the Si peak. Therefore, the additional Ti is thought to sit inertly on top of this intermixed overlayer.

Our results on the sputter-cleaned Si surface suggest a different interpretation for these results which does not require intermixing. From our LEED results, we know that as Ti is deposited, the long-range order of the surface layer is lost, suggesting that the Si atoms at the surface are displaced from their lattice positions, resulting in a loss of long-range order. This would account for the increase in the number of Si atoms visible to the ion beam and detector in the shadowing and blocking geometry. From our AES results, we know that the overlayer for a sputter-cleaned Si surface grows by island formation and that Si is still exposed at the top-most layer, even after the equivalent of 2 layers of Ti have been deposited. This would account for the absence of a shift of the highenergy onset of the Si peak in the ion backscattering results until more than 2-3 layers of Ti have been deposited. Si and Ti AES versus Ti deposition calculations for an intermixed Ti overlayer (with uniform thickness or with a Poisson distribution in thickness) are not consistent with the measured AES data.

VII. CONCLUSIONS

In direct contradiction with the results of previous studies, we find that it is possible to grow Ti on Si in the layer-by-layer mode at room temperature, and that there is no intermixing beyond (possibly) the first layer of Ti. The origin of this new finding lies first of all in the important effect of the cleaning procedure used to prepare the surface prior to Ti deposition. Secondly, we have observed a structural disruption of the Si surfaces by submonolayer coverages of Ti that can explain observations that have previously been interpreted in terms of intermixing. On both Si(100) and Si(111) surfaces cleaned by heating only, the AES signal intensity versus Ti coverage clearly indicates layer-by-layer growth of Ti. The inelastic mean free path deduced from the measurements is 4.0 Å for the 90 eV Si $L_{2,3}VV$ electrons and 5.7 Å for the 385 eV Ti $L_3M_{2,3}M_{2,3}$ electrons. Measurements of the Ti 2p core edges via appearance potential spectroscopy reveal that the Ti overlayer takes on a metallic character at submonolayer coverages. These results show clearly that intermixing of the Ti with the Si substrate does not occur. However, the deposition of less than a monolayer of Ti causes the (1×1) LEED patterns of both the (100) and the (111) oriented substrates to disappear completely. This shows that in spite of the lack of intermixing, the Ti atoms seriously disrupt the Si lattice in the near-surface region.

Previous studies of the growth of Ti were carried out on Si surfaces cleaned by a combination of sputtering and heating. We find that using this cleaning procedure results in no difference in the LEED or APS result for Ti growth. The variation of the AES intensity, however, is far more gradual than for the heat-cleaned surface. Since the APS results are the same as for the heat-cleaned surface and totally different from those observed for the titanium-silicide layer formed by heating, this cannot be the result of intermixing. Instead the Ti must be growing in an island-forming mode on the sputter-cleaned surfaces. The growth curve can be fit well with no adjustable parameters using a Poisson distribution of Ti thickness and the inelastic mean free paths obtained from the layer-by-layer growth curves. If the growth curve is analyzed by the approximate exponential decay curve, an apparent mean free path of 8 Å is obtained for the 90 eV Si $L_{2,3}VV$ electrons, consistent with previous results on the sputter-cleaned surface.

These results show the importance of surface preparation in determining overlayer growth mechanisms. The disruption of the Si lattice by the Ti overlayers signals the strength of the Ti-Si interaction, and must serve as the initiating step for silicide formation. This disruption of the Si lattice may be responsible for ion-backscattering results that were interpreted as being due to Ti-Si intermixing. Neither our studies of the growth mode nor of the Ti core levels via APS support the possibility of intermixing at room temperature.

ACKNOWLEDGMENTS

We wish to thank Dan Abell for his assistance in the AES measurements. J. V. thanks Tekniikan Edistämissäätiö, Emil Aaltonen Foundation, and Tauno Tönning Foundation for financial support. Computer facilities were provided by the Computer Science Center of the University of Maryland. This work was supported by Martin Marietta Laboratories and the National Science Foundation under Grant No. DMR-83-51436.

²K. N. Tu and J. W. Mayer, in *Thin Films-Interdiffusion and Reactions*, edited by J. M. Poate, K. N. Tu, and J. W. Mayer

¹S. P. Murarka, *Silicides for VLSI Application* (Academic, New York, 1983), and references therein.

⁽Wiley, New York, 1978), p. 359.

³F. W. Glaser and D. Toskowitz, Powder Metall. Bull. 6, 178 (1953).

⁴M. Wittmer and K. N. Tu, Phys. Rev. B 29, 2010 (1984).

- ⁵Marc A. Taubenblatt and C. R. Helms, J. Appl. Phys. **53**, 6308 (1982).
- ⁶Marc A. Taubenblatt, Douglas Thomson, and C. R. Helms, Appl. Phys. Lett. **44**, 895 (1984).
- ⁷S. P. Murarka and D. B. Fraser, J. Appl. Phys. 51, 342 (1980).
- ⁸L. S. Hung, J. Gyulia, J. W. Mayer, S. S. Lau, and M.-A. Nicolet, J. Appl. Phys. 54, 5076 (1983).
- ⁹A. Cros, C. Pirri, and J. Derrien, Surf. Sci. 152, 1113 (1985).
- ¹⁰A. S. Wakita, T. W. Sigmon, and J. F. Gibbons, Appl. Phys. Lett. **45**, 140 (1984).
- ¹¹M. C. Burrell and T. R. Armstrong, J. Vac. Sci. Technol. A 1, 1831 (1983).
- ¹²R. Butz, G. W. Rubloff, T. Y. Tan, and P. S. Ho, Phys. Rev. B 30, 5421 (1984).
- ¹³E. J. van Loenen, A. E. M. J. Fischer, and J. F. van der Veen, Surf. Sci. 155, 65 (1985).
- ¹⁴M. Iwami, S. Hashimoto, and A. Hiraki, Solid State Commun. 49, 459 (1984).
- ¹⁵A. Franciosi and J. H. Weaver, Physica 117B & 118B, 846 (1983); and Surf. Sci. 132, 324 (1983).
- ¹⁶E. J. van Loenen, M. Iwami, R. M. Tromp, and J. F. van der Veen, Surf. Sci. 137, 1 (1984).
- ¹⁷J. J. Lander and J. Morrison, Surf. Sci. 2, 553 (1964).
- ¹⁸B. T. Jonker, J. F. Morar, and R. L. Park, Phys. Rev. B 24, 2951 (1981).
- ¹⁹R. L. Park and J. E. Houston, J. Vac. Sci. Technol. 11, 1 (1974).

- ²⁰J. Kirschner and P. Staib, Appl. Phys. 6, 99 (1975).
- ²¹E. Bauer, H. Poppa, G. Todd, and P. R. Davis, J. Appl. Phys. **48**, 3773 (1977).
- ²²R. A. Armstrong, Surf. Sci. 50, 615 (1975).
- ²³M. P. Seah, Surf. Sci. 32, 703 (1972).
- ²⁴A value for the IMFP is also obtainable from the slopes of the linear segments of the AES-versus-Ti-deposition curve, but such a method is more difficult and more sensitive to errors in slope than the least-squares fit through the intersection points. The values obtained are comparable.
- ²⁵F. Pons, J. LeHericy, and J. P. Langeron, Surf. Sci. **69**, 565 (1977).
- ²⁶R. Butz, G. W. Rubloff, and P. S. Ho, J. Vac. Sci. Technol. A 1, 771 (1983).
- ²⁷J. G. Clabes, G. W. Rubloff, and T. Y. Tan, Phys. Rev. B 29, 1540 (1984).
- ²⁸Y. U. Idzerda, J. Vähäkangas, E. D. Williams, and R. L. Park (unpublished).
- ²⁹John A. Roth and C. R. Crowell, J. Vac. Sci. Technol. 15, 1317 (1978).
- ³⁰Robert L. Park and J. E. Houston, Phys. Rev. B 6, 1073 (1972).
- ³¹P. J. Feibelman, J. A. Appelbaum, and D. R. Hamann, Phys. Rev. B 20, 1433 (1979).
- ³²J. Vähäkangas, E. D. Williams, and R. L. Park, Phys. Rev. B 33, 2281 (1986).