Reaction and structure of Ti on Si probed by surface extended energy-loss fine structure and extended appearance potential fine structure

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The local structures of the low-temperature (< 500 °C) phases of the Ti/Si system have been determined by surface extended energy-loss fine structure (SEELFS) and by extended appearance potential fine structure (EAPFS), two variations of the electron analog of x-ray absorption fine structure (EXAFS). The extended fine structure above the Ti L_{23} edge has been measured for thin layers of Ti deposited on atomically clean Si surface and annealed at 20 °C (a pure Ti overlayer), 250 °C (a Si-rich Ti overlayer), and 400 °C (a silicide phase). Data were analyzed using standard EXAFS analysis routines including $\Delta l = +1$ phase shifts, resulting in peak positions at 2.93 ± 0.02 Å for the two unreacted phases and 2.39 ± 0.04 Å for the silicide phase. These values are in good agreement with the known spacings of bulk Ti and TiSi, respectively. The *ratio technique*, which avoids phase-shift difficulties, was applied to these measurements showing that the pure Ti overlayer and the Si-rich Ti overlayer have the same Ti–Ti spacing, but the Si-rich Ti overlayer exhibits a higher degree of disorder. We find no evidence for the formation of a Ti–Si bond in the Si-rich Ti overlayer. This first application of the ratio technique to SEELFS and EAPFS demonstrates its usefulness.

I. INTRODUCTION

The determination of the atomic structure at the transition metal–silicon interface has led to an increased understanding of the kinetics of silicide formation and to the electronic and structural properties of the silicides.[1] Although many techniques which depend on long-range order (LRO) of the sample [x-ray diffraction, transmission electron microscopy (TEM), medium-energy ion scattering (MEIS), low-energy electron diffraction (LEED), etc.] have been utilized, use of techniques which are sensitive to the short-range order (SRO) are less common. Measurement of extended fine structure (EFS) is a SRO technique which can determine the local atomic structure. Determination via electron emission provides the additional benefit of sensitivity to the near surface region. We report[2] the local structure determination for various phases of the Ti/Si system, whose initial growth and subsequent heat-induced silicide formation have been previously well characterized.[3,4] The local structure has been determined through surface extended energy-loss fine structure (SEELFS)[5–8] and extended appearance potential fine structure (EAPFS),[9–11] both electron based extended fine structure (EFS) techniques which offer much of the powerful analytic capabilities of extended x-ray absorption fine structure (EXAFS)[12–14] in an in-house laboratory setting. Both are local-structure probes sensitive to the near-surface region, and both can be implemented with commercially available electron sources and detectors. Electron-beam-based EFS methods can easily be modulated for lock-in detection and can also be focused to examine small regions and any inhomogeneities or defects on a microscopic scale. In most cases, the same facilities used for characterizing the surface/system can be used for the EFS measurement, simplifying experimental procedures.

Previously[3] we have studied the initial growth and subsequent reaction of Ti on Si(111) and Si(100) to establish methods for the manufacture and characterization of the various phases of the Ti/Si system.[3] We find that the initial growth of Ti on the Si surface is delicately dependent upon the surface cleaning procedure. For surfaces, cleaned only by heating to > 850 °C for 3 min to desorb the surface oxide, the growth mode is layer by layer (Frank–van der Merwe). If we use a different, though common,[15–17] surface cleaning procedure involving an Ar^+ ion sputtering and a subsequent 15-min anneal at 850 °C after the heat cleaning, the overlayer no longer grows layer by layer, but as islands (Volmer–Weber). Standard surface characterization techniques [LEED, Auger electron spectroscopy (AES)] show no differences between the two cleaned surfaces prior to deposition.

We have also characterized the composition and bonding of the heat reacted Ti/Si system.[4] Our results indicate that for thin films (10 layers or 25 Å) of Ti deposited on Si, as the substrate temperature is increased from room temperature to 850 °C, the silicon content of the overlayer increases. At ~400 °C and ~650 °C two stable silicide phases occur which we have tentatively identified as TiSi and $TiSi_2$, respectively. We find no evidence of silicide formation at the lower temperatures (~250 °C) where atomic intermixing begins. Earlier investigators[18] have similarly identified the lower-temperature silicide phase as having a stoichiometry near that of TiSi, but since the phase lacks long-range order, no prior structural identification has been made. A detailed examination of the local structure surrounding the Ti atom will unequivocally determine the silicide phase present, the extent of silicide formation, and perhaps indicate the method by which the Si diffuses.

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II. EXPERIMENT

The surface analysis system used for these experiments, as well as the sample preparation have been described previously.[2-4]

The extended appearance potential fine structure spectra were taken by the disappearance technique (DAPS),[19,20] using the LEED optics to measure the quasielastic scattering yield as the energy of the electrons incident on the sample is swept through the Ti $2p$ excitation thresholds and beyond the extended fine structure region ($\sim$400 eV). Only those electrons that had lost less than 10 eV of energy from the incident electron energy (quasielastically scattered electrons) were detected. The first derivative of the quasielastic yield was measured by applying a 10-V peak-to-peak modulation voltage to the sample potential and using lock-in detection techniques. Details of the surface extended energy-loss fine structure measurement have been described elsewhere.[5,7] In brief, the electron energy-loss spectrum for 1–2 keV normally incident electrons is measured at energies below an excitation loss threshold (in this case the Ti $L_{2,3}$ edge). Again lock-in detection techniques are used to measure the first (or second) derivative spectrum.

III. RESULTS

We have used SEELFS and EAPFS to measure the EFS beyond the Ti L_{23} edge (460-eV binding energy) for the as-deposited Ti overlayer, for a Ti overlayer annealed at 250 °C which exhibits a large Si concentration (30%) but no evidence of silicide formation, and for the silicide formed at 400 °C. All spectra were measured immediately after annealing with the sample at room temperature. The reduced EFS signal strength for the $TiSi_2$ overlayer formed at 650 °C, prevented us from obtaining analyzable EFS for that phase. The reduction in the amplitude of the core loss feature and associated EFS is directly related to the reduction in Ti content within the surface region due to the presence of a silicon concentration in excess of the stoichiometric value for $TiSi_2$ at the surface of the silicide layer. The reduction is most likely due to the presence of a pure Si region at the surface.[4,15] The SEELFS and the EAPFS of the Ti L_{23} edge for the three phases of the Ti/Si system measured are shown in Figs. 1 and 2, respectively. The sharp feature at 560 eV is the L_1 core loss feature. This sharp feature was included in the Fourier transform and presents no problem in our analysis because it contributes only to the high R spacings away from the first neighbor atomic spacing.

The analysis of the EFS needed to extract the local atomic spacing begins by isolating the EFS features through data truncation and a cubic-spline background subtraction. After the EFS is isolated, it is integrated (if necessary) to obtain the undifferentiated electron loss spectrum for SEELFS and the first derivative electron energy spectrum for EAPFS. These electron energy spectra are the proper forms required for strict analogy with EXAFS.[21] First- and second-derivative SEELFS spectra have been utilized to obtain "pseudoradial distribution functions" (PRDF's)[7,22] which reproduce known atomic spacings,[6,8] but these PRDF's intensify higher coordination shell contributions. The energy spectra were

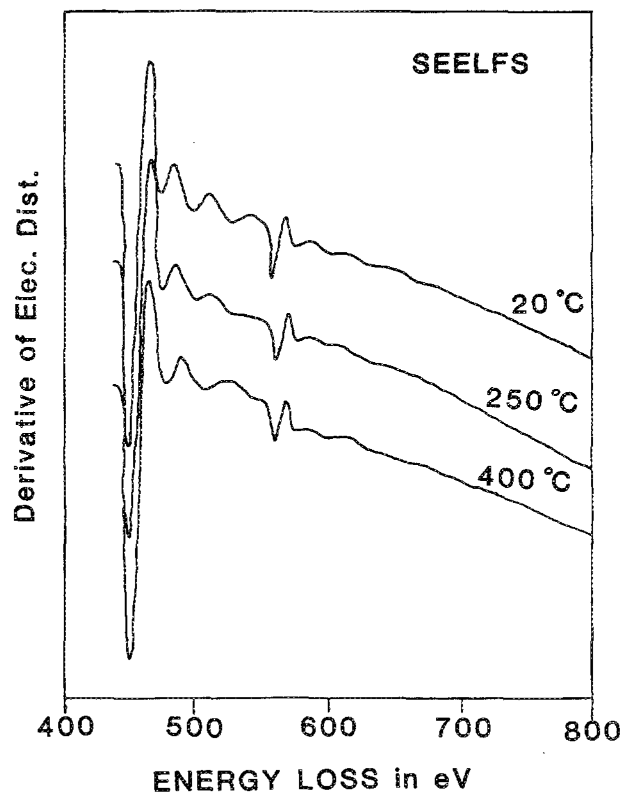

FIG. 1. First derivative SEELFS measured EFS above the Ti L_{23} edge for three phases of the Ti/Si system: (a) 20 °C pure Ti overlayer, (b) 250 °C Si-rich Ti overlayer, and (c) 400 °C TiSi film. Each has been normalized to the measured L_{23} core loss intensity. The sharp feature at the loss energy of 560 eV is the L_1 core loss feature.

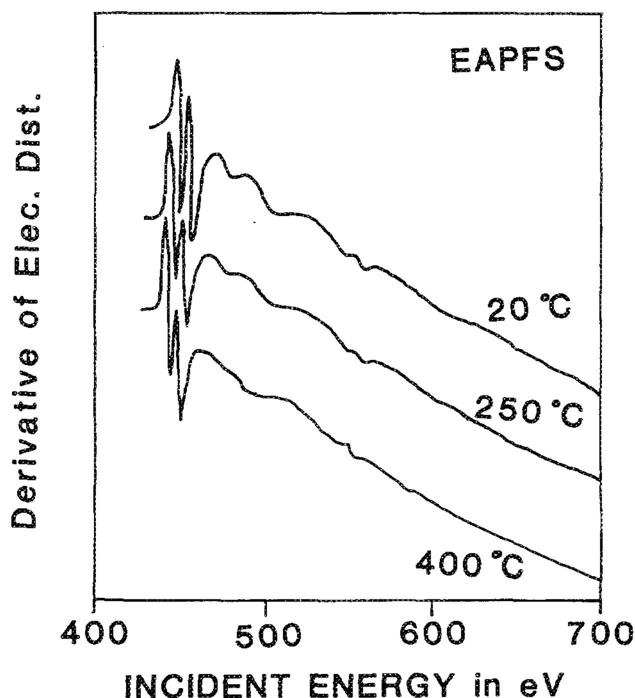

FIG. 2. First derivative EAPFS measured EFS above the Ti L_{23} edge for three phases of the Ti/Si system: (a) 20 °C pure Ti overlayer, (b) 250 °C Si-rich Ti overlayer, and (c) 400 °C TiSi film. Each has been normalized to the measured L_{23} core loss intensity. The sharp feature at the loss energy of 560 eV is the L_1 core loss feature.

converted to wave number data with a k range of 2.5–9 $Å^{-1}$, comparable to SEXAFS k ranges. Using standard calculated phase shifts for the Ti central atom, assuming $l = 2$ ($\Delta l = +1$),[23] and the Lee–Beni method for the determination of E_0,[24] we analyzed the undifferentiated SEELFS and first-derivative EAPFS spectra to obtain radial distribution functions which represent the interatomic spacings[25,26] (shown in Fig. 3). The similarity between the RDF's measured by SEELFS and by EAPFS for each different phase is apparent.

For the pure Ti overlayer *and* the 250 °C Si-rich Ti overlayer, the first nearest-neighbor separation occurs at 2.93 ± 0.02 Å. This value is in agreement with other EFS measurements for the Ti L_{23} edge (SEELFS[27] and EXAFS[28]). Crystallographic measurements on pure Ti indicate that there should be two interatomic spacings very near each other at 2.89 and 2.94 Å,[29] both with a coordination number of 6. These peaks would be unresolved and appear as one peak at 2.915 Å. For the silicide formed at 400 °C, the nearest-neighbor spacing is 2.39 ± 0.04 Å. This is in good agreement with the value expected for TiSi. All three bulk structures of TiSi have two nearby Ti–Si atomic spacings at 2.30 and 2.44 Å, each with the same coordination number.[29]

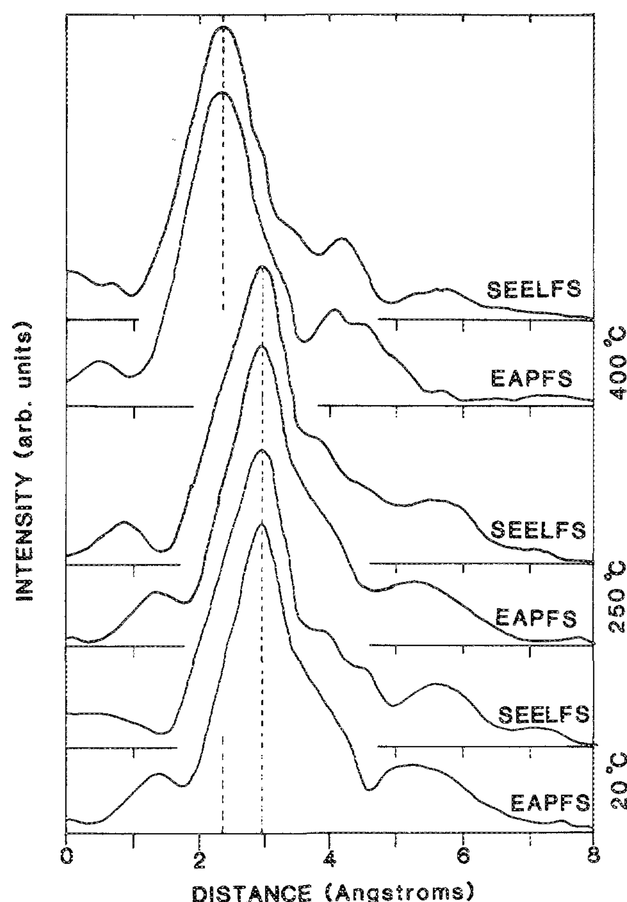

FIG. 3. Calculated RDF's for the undifferentiated SEELFS and first-derivative EAPFS measured EFS for three annealing temperatures: 20 °C pure Ti overlayer, 250 °C Si-rich Ti overlayer, and 400 °C TiSi film. Calculations include $l = 2$ phase-shift corrections (dipole approximation). First peak positions are the same for both the SEELFS and EAPFS RDF's and occur at $R = 2.93 \pm 0.04$ Å for the 20 °C and the 250 °C annealed films and at $R = 2.39 \pm 0.04$ Å for the 400 °C annealed film.

If these two spacings are not resolved in the EFS measurement, an apparent spacing of 2.37 Å would be measured. For comparison, the nearest-neighbor bond in $TiSi_2$ is a Ti–Si bond at 2.54 Å. Our results indicate that the 400 °C annealed thin film is predominantly TiSi and not a mixture of silicide phases as has been suggested.[16,30] To differentiate between the three possible reported phases of TiSi, information at much higher atomic spacings would be needed. We are currently unable to make this differentiation via EFS (though information contained in the unanalyzed near edge structure may provide this ability).

The results for the film heated to 250 °C, show no evidence for the formation of a Ti–Si bond. The Ti interatomic spacing remains the same as for pure Ti. Additional information about the 250 °C annealed phase can be obtained through the application of the ratio technique. In this analysis technique, we compare the measured EFS from a material of known structure against the measured EFS of our unknown. By comparing the relative amplitude and phase of the EFS of the standard and the unknown, we can establish the atomic spacing difference, coordination number difference, and relative disorder of the two. In this case the pure Ti overlayer serves as the standard to which the 250 °C annealed overlayer is compared. In Fig. 4 we show the total phase difference versus wave number for the pure Ti overlayer (20 °C) and the Si-rich overlayer (250 °C). The values for E_0 have been chosen to also require that the extrapolated straight-line fit to the phase difference be zero at $k = 0$. From the slope of this curve we can determine the atomic spacing difference ΔR. We find ΔR ($\Delta R = R_{\text{pure Ti}} - R_{\text{Si-rich Ti}}$) is zero within our uncertainty (± 0.04 Å). The presence of Si in the Ti overlayer has not changed the Ti structure. There is no evidence for the formation of a Ti–Si bond at either the Ti–Si interatomic spacing (present if a silicide is formed) or at the Ti–Ti interatomic spacing (as would occur if a significant fraction of the Ti was substituted by the Si). Simple computer simulations suggest that substitutional Si concentrations of lower than 20% would be detectable.

We can also compare the relative amplitudes of the standard and unknown by examining the log ratio of the EFS amplitude of the two. Figure 5 shows a better than typical

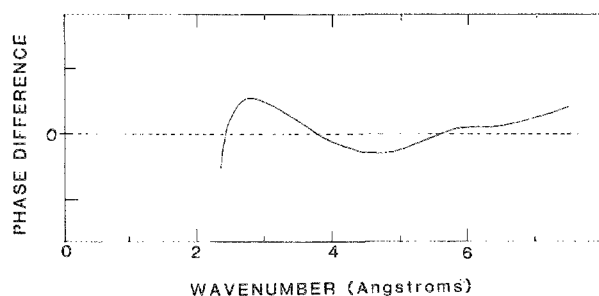

FIG. 4. Total phase difference between first shell EFS for pure Ti overlayer (20 °C) and 250 °C annealed Si-rich Ti overlayer vs wave number. The EFS is taken from undifferentiated SEELFS above the Ti L_{23} edge. Values for E_0 have been selected that require that the extrapolated straight line be zero at $k = 0$. The slope of the straight line, which is the difference in atomic spacings, is -0.01 Å.

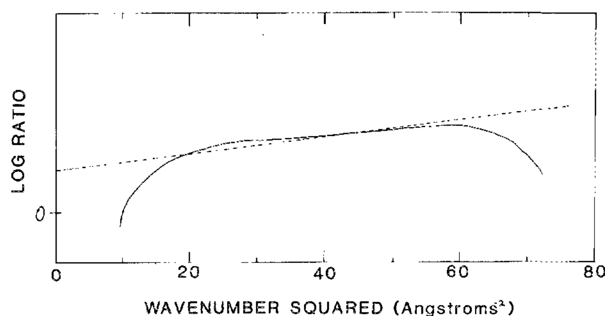

FIG. 5. Log of the ratio of the amplitude of the first shell EFS for the as-deposited pure Ti overlayer (20 °C) and the 250 °C annealed Si-rich Ti overlayer vs the square of the wave number. The slope indicates the change in the square of the Debye–Waller factor. The slope is − 0.007.

plot of the log ratio of the amplitude of the EFS for the pure Ti overlayer and the Si-rich Ti overlayer annealed at 250 °C. The slope of the straight-line fit gives a value for the difference in the Debye–Waller-type Gaussian disorder. For Fig. 5, we find $\Delta\sigma^2 = \sigma^2_{\text{pure Ti}} - \sigma^2_{\text{Si-rich Ti}} = -0.007 \pm 0.004$ Å^2. Such a value for the Gaussian disorder difference indicates that the Si diffusion into the Ti overlayer creates some structural disruption of the Ti crystalline lattice. Furthermore, the quality of the fit to a straight line indicates that the backscattering element is the same for the pure Ti overlayer (a Ti backscattering atom) and the Si-rich Ti overlayer (where the backscattering atom could conceivably be either Ti or Si). The absence of the appearance of a Ti–Si bond implies that the Si diffusion is via grain boundaries and is not interstitial, substitutional, or by silicide formation. Extraction of coordination numbers from our amplitude analysis was complicated by EFS normalization considerations.

The amplitude comparison was made for a number of samples annealed at 250 °C. In all cases, there was an increase in σ^2 ranging from 0.005 to 0.014 Å^2. Increasing the Si content of the films to as large as ~40% by heating to 300 °C resulted in increases in σ^2 within the same range. This relative insensitivity of the disorder to the amount of Si in the Ti film is further evidence for grain boundary diffusion.

IV. SUMMARY

In this and preceding studies,[3,4] we have characterized the growth and reaction of Ti thin films with a Si substrate. Small quantities of Ti deposited at room temperature disrupt the structural order of at least the top three layers of Si. However, there is no evidence for intermixing beyond possibly the first layer, and no evidence for any silicide formation. Heating to temperatures up to ~300 °C results in diffusion of Si into the Ti layer, still with no evidence of silicide formation. Analysis of the EFS shows that the Si is neither interstitial or substitutional on the Ti lattice, but does cause some increase in the disorder of the Ti film. This strongly suggests that the Si migrates via grain boundary diffusion.[18] A stable silicide with approximate stoichiometry is formed at ~400 °C. The structure of this phase had not been determined previously because it is poorly ordered. However, EFS measurements show that the nearest-neighbor Ti–Si spacing in this film is 2.39 ± 0.04 Å, consistent with the known value of bulk TiSi. Upon heating near 650 °C, a second stable silicide phase is formed. Its stoichiometry is consistent with a $TiSi_2$ film[15] with a Si-rich surface region.[4] At higher temperatures the Si content increases near the surface with possible[18] agglomeration of the silicide into islands.

It is clear from these results that the addition of EFS measurements to more conventional surface analytical techniques greatly expands the amount of information obtainable concerning thin film growth and reaction. The use of an electron-beam-based EFS technique, as in this study, provides reliable information using only existing surface analysis equipment.

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