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Structural investigation of the initial interface region formed by thin titanium films on silicon (111)

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A structural study of the initial interface region formed by titanium on silicon (111) was undertaken. Thin films (100 Å) of titanium were deposited in ultrahigh vacuum (UHV) conditions onto atomically clean silicon(111) wafers and annealed *in situ* at 25 °C intervals between 300 and 475 °C. Structural characterization of the evolving interface was performed primarily via extended x-ray absorption fine structure (EXAFS) measurements. Results indicate that a major structural rearrangement takes place between 400 and 425 °C. EXAFS fitting analysis reveals this transition to be from a disordered TiSi-like phase to a more ordered C49-like disilicide state. The results are compared with those previously reported for the zirconium:silicon system. © *1996 American Institute of Physics.* [S0021-8979(96)01813-0]

I. INTRODUCTION

The refractory metal silicides are attractive to the electronics industry due to their low resistivities and relatively good stability to high temperature processing. In thin film form, these silicides can be utilized as highly conducting contacts on silicon substrates. Titanium, which forms the lowest resistivity silicide ($TiSi_2$, 13–16 $\mu\Omega$),[1] has been the subject of many studies in both its stable orthorhombic face centered C54 phase and its metastable orthorhombic base centered C49 phase.[2–6] The low surface/interface free energy C49 phase is known to transform to the C54 phase, which has a lower bulk free energy, at temperatures of around 700 °C.[5–8] In a previous study by the authors,[9] a structural investigation of the initial interface region formed by thin zirconium films on silicon (111) was undertaken. Since zirconium only exhibits a C49 phase disilicide, this suggested that alloying small quantities of zirconium with titanium may stabilize the epitaxial C49 $TiSi_2$ phase at higher temperatures without considerably increasing the resistivity. Both titanium and zirconium have been reported to show a highly disordered interface region at low annealing temperatures.[3,10–16] Since the knowledge and comparison of the microstructure of such intermediate layers is important to the understanding of the formation of the crystalline titanium silicide or alloy silicide, we have investigated the structural changes associated with the titanium:silicon interface at relatively low annealing temperatures using extended x-ray absorption fine structure (EXAFS) measurements.

II. SAMPLE PREPARATION AND CHARACTERIZATION

To make a direct and meaningful comparison with previous work[9] identical conditions were used. Titanium films of 100 Å thickness were electron beam evaporated in ultrahigh vacuum (10^{-9}–10^{-10} Torr) onto 25.4 mm diam *n*-type single crystal Si (111) wafers held at ambient temperature. The silicon had previously been subject to UV/ozone irradiation to remove hydrocarbons and a HF/alcohol based spin etch to remove the native oxide. The wafers were then immediately inserted into vacuum and further cleaned by heating to 900 °C for 10 min to desorb hydrogen and other residues. The resulting surfaces all exhibited a 7×7 Si (111) reconstructed low-energy electron-diffraction (LEED) pattern showing them to be atomically clean. Depositions were monitored by a quartz-crystal oscillator. *In situ* Auger electron spectroscopy (AES) indicated no significant interdiffusion of the silicon at room temperature. The samples were subsequently annealed *in situ* for 20 min at temperatures between 300 and 475 °C.

III. EXAFS EXPERIMENTS AND DATA ANALYSIS

X-ray absorption experiments on the Ti *K* edge (4966 eV) were performed on beamline X11A of the National Synchrotron Light Source using low-angle total electron yield detection[17] in an arrangement where the samples could be tilted or rotated with respect to the beam to try to minimize Bragg reflections.[18] The synchrotron electron beam energy was 2.58 GeV and the stored current was between 110 and 210 mA. The x-ray energy was defined by a double crystal monochromator with Si (111) crystals. The energy calibration was monitored periodically with a transmission scan of a titanium foil. Harmonics were rejected by detuning the crystals with respect to one another resulting in a 60% decrease in the incident x-ray intensity.

The EXAFS data pre- and postedge backgrounds were removed by fitting smooth, low order polynomials to the appropriate regions of the experimental spectra using the Eindhoven routines.[19] During this procedure, any obvious Bragg peaks (e.g., high amplitude, narrow peaks) from the crystalline substrate were also removed. Structural information was obtained by a nonlinear least squares fitting of the theoretical EXAFS function (χ) to the experimental data using the rapid curved wave theory of EXAFS[20] as implemented in the program EXCURV88.[21] Backscattering factors for the titanium and silicon atoms were theoretically generated by the program. The theoretically generated phase shifts were empirically modified by fitting to the standard compound $TiSi_2$ (C54 phase) so that the structural parameters

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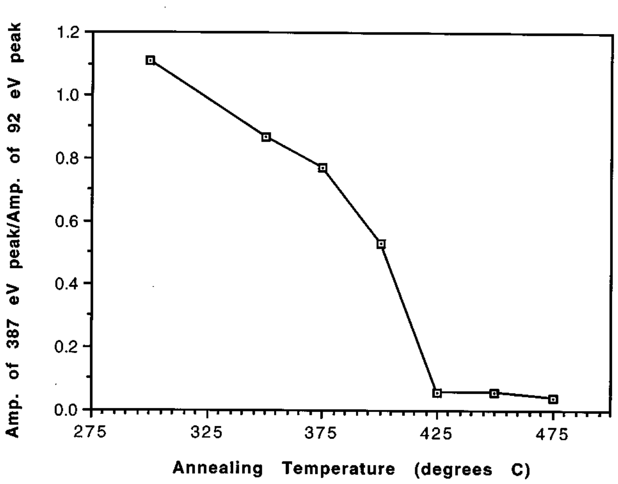

FIG. 1. The ratio of the 387 eV (Ti) Auger electron spectroscopy peak and the 92 eV (Si) peak vs annealing temperature. The rapid reduction in the amplitude of the Ti peaks at around 425 °C is indicative of a major structural rearrangement.

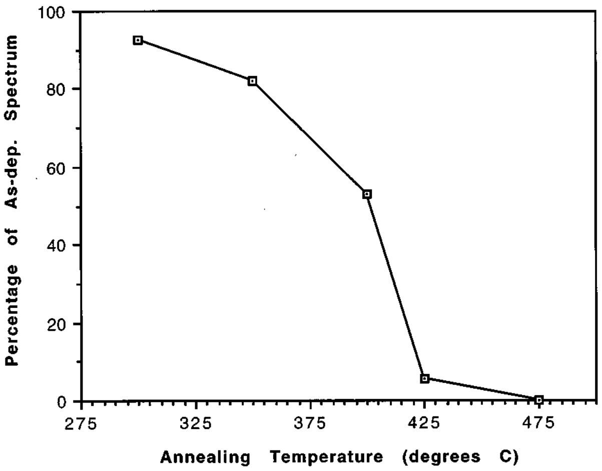

FIG. 2. Results of fitting the titanium near-edge data for 100 Å Ti on Si (111) with a linear combination of the data collected from an as-deposited sample and a sample annealed at 475 °C. A major structural rearrangement appears to take place around 425 °C.

agreed, to within experimental error, with the accepted values. The amplitude factor (which is used to account for absorption events that do not result in EXAFS, such as multielectron excitations) was set at 0.8. The photoelectron mean free path, described in terms of an imaginary part of the potential in the fits, was allowed to float around the value obtained for the $TiSi_2$ standard sample (-8.5 eV) and ranged from -8.3 to -9.8 eV, generally becoming less negative with increasing annealing temperature. These values are typical for such a system. The energy offset (a nonstructural parameter which is used in the fitting routine to correct for the energy offset of the photoelectron at zero wave vector) was allowed to float during the fitting and varied from 10.43 to zero, generally decreasing with increasing annealing temperature. The limit of significance of correlated parameters was calculated statistically within the EXCURV88 program[22] and plotted as a broad line on contour maps of the fit index over a range of parameter values. This method is extremely helpful in indicating the degree of any correlation and estimating the real errors involved. It is the average error estimates derived from such contour plots that are quoted in this article.

IV. RESULTS

After deposition and annealing, *in situ* Auger electron spectroscopy (AES) was performed on all samples. The ratio of the 387 eV Ti AES peak to the 92 eV Si peak is plotted in Fig. 1, where the rapid reduction in the amplitude of the Ti peaks (indicative of a major structural rearrangement) is seen at around 425 °C. The results from fitting the titanium x-ray absorption near-edge structure (XANES) with a linear combination of the data collected from the as-deposited sample and a sample annealed at 475 °C (the highest annealing temperature) are shown in Fig. 2. This plot looks remarkably similar to the Auger results in Fig. 1 and again points to some major structural rearrangement having taken place around 425 °C.

The k^2-weighted Ti K-edge EXAFS spectra of the samples are shown in Fig. 3. Spectra from the $TiSi_2$ [C54] standard compound and a sample previously determined to be $TiSi_2$ [C49]-like by EXAFS[23] are also shown for comparison. The corresponding k^2-weighted Fourier transforms taken over the range 3–10.5 $Å^{-1}$ and with a Hanning window value of 0.1 are shown in Fig. 4. A typical k-space fit to a k^2-weighted spectrum is shown in Fig. 5. Results of fitting to the EXAFS data are presented in Table I, where R repre-

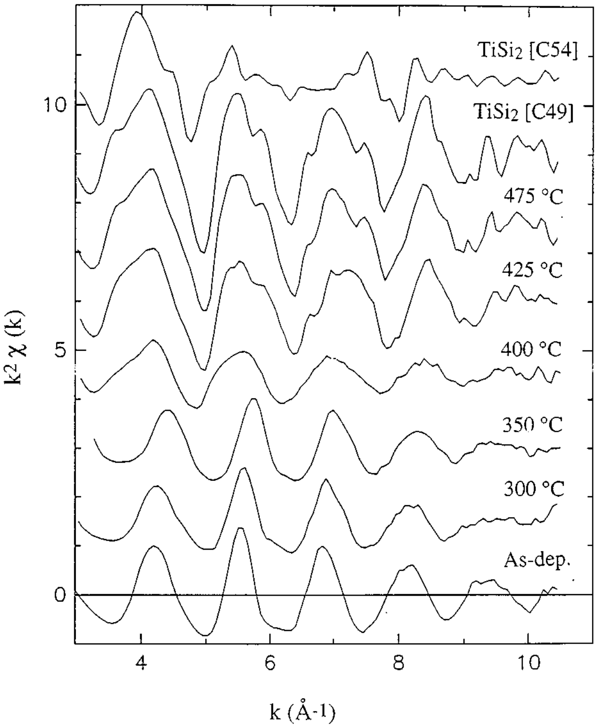

FIG. 3. The k^2-weighted Ti K-edge experimental EXAFS spectra of 100 Å Ti on Si (111) annealed at temperatures between 300 and 475 °C. Spectra from the $TiSi_2$ [C54] standard compound and a $TiSi_2$ [C49]-like sample are shown for comparison. The data are offset for clarity.

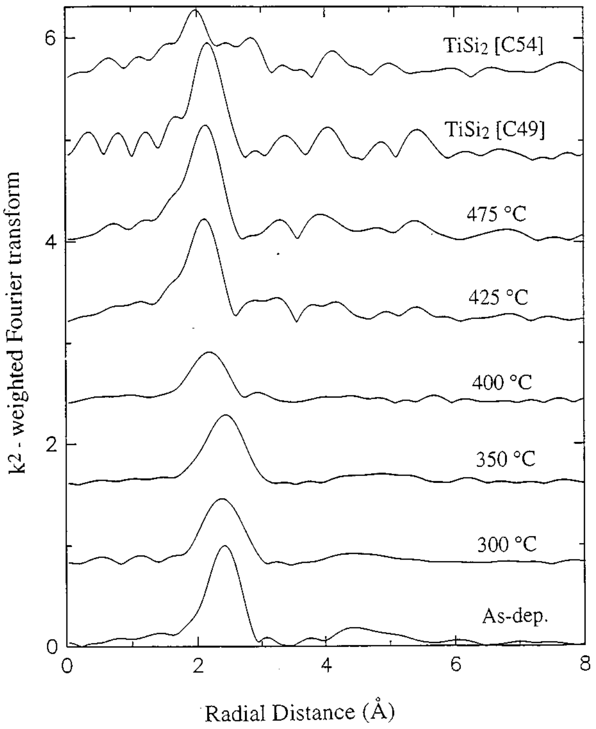

FIG. 4. The k^2-weighted Fourier transforms of the EXAFS data shown in Fig. 3, taken over the k-space range 3–10.5 $Å^{-1}$ with a Hanning window value of 0.1. The data are offset for clarity.

sents the average shell radius, N the number of neighboring atoms in that shell, A is a Debye–Waller factor giving a measure of the static and thermal disorder in the structure. Values in parentheses are theoretical (generated with the crystal modeling program, ISTRUC) and shown for comparison. From the spectra, one can see that the samples annealed at 300 and 350 °C are very similar to the as-deposited sample (which has a first Ti–Ti shell at around 2.88 Å), but with a slightly reduced first shell interatomic distance of 2.79 Å and a reduced first shell coordination (3.8 and 4.1, respectively, as opposed to 6 for the metal). In contrast, the samples annealed at 425 and 475 °C exhibit similar spectra to the C49 phase (which has 10 Si atoms at around 2.70 Å and 6 Ti atoms at around 3.52 Å). While the first shell interatomic distances of these two samples are, in fact, closer to the nearest-neighbor Ti–Si distance in the C54 phase $TiSi_2$, the high first shell coordination number along with the greater than 3.5 Å second shell Ti–Ti distance (as opposed to the 2.75 Å Ti–Si distance for the C54 phase) indicate that these samples are, indeed, more C49-like in nature as the visual interpretation suggests. The coordination numbers in the first shell (Ti–Si) of these two annealed samples are close to the theoretical value, but those in the second shell (Ti–Ti) are reduced. For the highly disordered-looking 400 °C spectrum, least-squares fitting of the EXAFS data returned first shell parameters of 6.1 Si atoms at 2.63 Å, which is in close agreement with the theoretically generated parameters for TiSi [BFe structure] (6 Si atoms at 2.64 Å) which are shown in Table I for comparison. This is consistent with the XANES data which indicated this sample to be an almost equal mix of the Ti metal-like and $TiSi_2$ [C49]-like structures and the AES results of Fig. 1 which show the ratio of Ti to Si peaks to be 50:50 at 400 °C. While the XANES spectrum for this temperature still showed a residual pre-edge peak indicative of the metal, EXAFS fitting to the full data range could not place any Ti–Ti shells at distances corresponding to those in Ti metal.

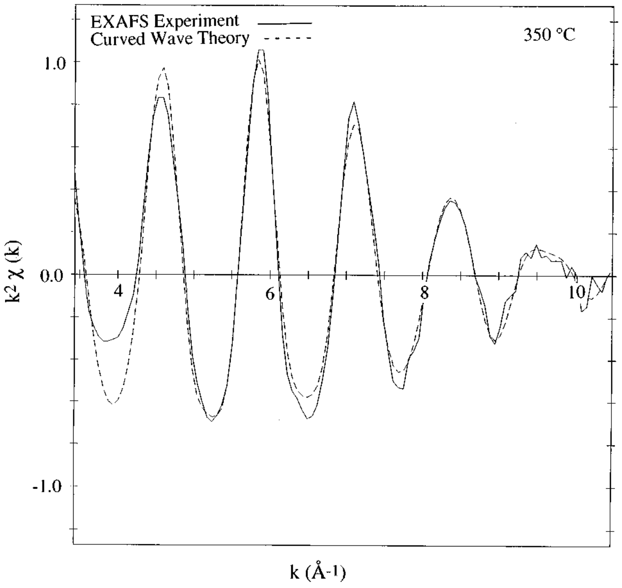

FIG. 5. A typical k-space fit to the k^2-weighted EXAFS data of 100 Å Ti on Si (111) annealed at 350 °C.

V. DISCUSSION

EXAFS, AES, and XANES results all indicate little reaction of the titanium and silicon on deposition and up to annealing temperatures of 350 °C. This lack of reaction at room temperature has been observed by others studying the initial reaction at the Ti/Si interface.[24] However, the aforementioned study used various, but all thinner initial titanium film coverages than in the present investigation and reported initial intermixing of the titanium and silicon as low as 250 °C.

The first non titanium-like structure was observed by EXAFS at an annealing temperature of 400 °C. As can be evidenced by the EXAFS spectrum and the large first shell Debye–Waller factor in Table I, this structure is highly disordered. The presence of a highly disordered or even an amorphous titanium:silicon interlayer has been noted in many studies[3,12,25,26] and there are other, important similarities to existing work. Both XANES and AES results indicated the 400 °C annealed sample to be an almost equal mix of titanium and silicon. Holloway and Sinclair[25] estimated the composition of their amorphous Ti–Si alloy to be roughly equiatomic while Raaijmakers *et al.*[3] determined the composition of their amorphous $TiSi_x$ to be $0.9<x<1.2$. Other authors, including some of those who reported a disordered Ti–Si phase, saw evidence of a crystalline monosilicide.[2,10–12,24,26] Indeed, the EXAFS fitting indicates that the first shell results of the 400 °C annealed sample are in close agreement with those for the BFe structure of crys-

TABLE I. Results of EXAFS fitting to Ti K-edge data.

Anneal Temp.	$R_{\text{Ti-Ti}}$ (Å)±0.01	$N_{\text{Ti-Ti}}$ ±1.5	$A_{\text{Ti-Ti}}$ (Å^2)±0.005	$R_{\text{Ti-Ti}}$ (Å)±0.5	$N_{\text{Ti-Ti}}$ ±3	$A_{\text{Ti-Ti}}$ (Å^2)±0.01	$R_{\text{Ti-Ti}}$ (Å)±0.02	$N_{\text{Ti-Ti}}$ ±4	$A_{\text{Ti-Ti}}$ (Å^2)±0.01
Ti metal	(2.88)	(6)	⋯	(2.92)	(6)	⋯	(4.10,4.67, 5.04)	(6,2, 18)	⋯
Room	2.88	7.3	0.012	2.93	4.1	0.017			
300 °C	2.79	3.8	0.001	2.94	4.3	0.001	5.07	24.3	0.029
350 °C	2.79	4.1	0.002	2.94	3.9	0.000	5.02	8.3	0.017
Anneal Temp.	$R_{\text{Ti-Si}}$ (Å)±0.01	$N_{\text{Ti-Si}}$ ±1.5	$A_{\text{Ti-Si}}$ (Å^2)±0.003	$R_{\text{Ti-Ti}}$ (Å)±0.02	$N_{\text{Ti-Ti}}$ ±2	$A_{\text{Ti-Ti}}$ (Å^2)±0.01	$R_{\text{Ti-Si}}$ (Å)±0.02	$N_{\text{Ti-Si}}$ ±3	$A_{\text{Ti-Si}}$ (Å^2)±0.01
TiSi [BFe]	(2.64)	(6)	⋯	(3.22,3.63)	(6,2)	⋯			
400 °C	2.63	6.1	0.016	3.6	0.6	0.000			
425 °C	2.57	8.2	0.009	3.56	2.3	0.000	4.49	14.9	0.019
475 °C	2.60	10.3	0.012	3.58	1.7	0.000	4.50	18.5	0.017
$TiSi_2$ [C49]	(2.70)	(10)	⋯	(3.52)	(6)	⋯	(4.53)	12	⋯
$TiSi_2$ [C54]	2.55	5.4	0.008	2.75 Ti–Si	5.8 Si	0.011 Ti–Si	3.20 Ti–Ti	2.7 Ti	0.005 Ti–Ti
	(2.54)	(4)	⋯	(2.75)	(6)	⋯	(3.20)	(4)	⋯

talline TiSi. In contrast to other work, our results do not indicate the presence of any Ti_5Si_3[27,28] which would have a mixed first shell of two titanium atoms at 2.56 Å and four silicon atoms at 2.67 Å (assuming that atoms less than about 0.25 Å apart would appear as an irresolvable single shell[29]).

Both AES and XANES fitting indicated a major structural rearrangement at around 425 °C and from the EXAFS spectra and fitting we can see that a C49-like phase has evolved. It is now important to compare this reaction sequence to the analogous work previously performed on the zirconium:silicon interface.[9] Here, while no reaction was indicated on deposition, reaction of the zirconium and silicon was seen even at the lowest annealing temperature (300 °C) resulting in a disordered–intermixed phase and no evidence was seen of any remaining metallic zirconium. In this case, the major structural rearrangement evidenced by AES and XANES fitting occurred around 350–375 °C and EXAFS fitting indicated this to be the nucleation of the first ordered state which had evolved into a ZrSi-like structure by 425 °C.

By 425 °C in the current study, the C49 phase $TiSi_2$ structure has already nucleated indicating that the reaction sequence occurs much faster and at a lower temperature for titanium than for zirconium. However, it is not initiated until a higher temperature than for zirconium. The TiSi-like phase is less ordered than its ZrSi counterpart and while it forms at a higher temperature, it transforms to the C49 phase at a lower temperature than for the zirconium system. In the latter case, the dominant structural rearrangement in the same annealing temperature range was the nucleation of ZrSi rather than the nucleation of the C49 phase disilicide. Hence, while the reaction paths are similar for these two systems, the titanium never quite forms such a stable and ordered monosilicide as does zirconium.

VI. CONCLUSIONS

We have reported EXAFS results on 100 Å films of titanium deposited on Si(111) and annealed to moderate temperatures (300–475 °C). The EXAFS fitting results suggest that a disordered TiSi-like phase forms as a precursor to the $TiSi_2$ C49 phase in this system. In this respect, zirconium and titanium do appear to follow similar structural reaction paths when annealed on Si (111) and this suggests that alloying small amounts of zirconium with titanium to stabilize the C49 structure would be possible. Indeed, alloy films of titanium and up to 20% zirconium have already been prepared by codeposition onto silicon (111) in this laboratory, and the resulting C49 phase alloys have proved to be more ordered and stable to higher temperatures than C49 phase $TiSi_2$.[30,31]

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