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

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A structural study of the initial interface region formed by zirconium on silicon (111) was undertaken. Thin films (100 Å) of zirconium were deposited in ultrahigh-vacuum conditions onto atomically, clean silicon (111) wafers and annealed *in situ* at 25 °C intervals between 300 and 425 °C, over which range Auger spectroscopy indicated silicon diffusion to the surface. 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 350 and 375 °C. EXAFS fitting analysis reveals this transition to be from a disordered-intermixed phase to a more ordered state having interatomic distances closely resembling those of ZrSi, but lower coordination numbers. Ordering continues with progressively higher annealing temperatures until the interface region assumes the ZrSi structure at ~425 °C. The results are discussed in terms of the free energy and strain of the interface film.

I. INTRODUCTION

The refractory metal silicides are attractive to the electronics industry due to their low thin-film 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 film¹ (13-16 $\mu\Omega$ cm), has been the object of many studies.²⁻⁶ However, the commonly resulting epitaxial silicide (TiSi₂) is often of the C49 phase and is, unfortunately, metastable-transforming to the stable C54 phase at temperatures of around 700 °C.^{5,6} Zirconium, however, only exhibits a C49 phase disilicide, and, being in the same periodic group, is chemically similar to titanium, affording the possibility of alloying small quantities of zirconium with titanium, in order to stabilize an epitaxial C49 structure at all temperatures. Among the refractory disilicides, those of zirconium and molybdenum have the lowest Schottky barrier height on n-type silicon (0.55 eV), but zirconium disilicide also has a relatively low film resistivity¹ $(35-40 \ \mu\Omega \text{ cm})$. The origin of this low resistivity is thought to be closely related to the microscopic structure at the interface.

The structural evolution of the silicide is obviously an important factor in the fabrication of epitaxial contacts. Both titanium and zirconium have been reported to show a highly disordered interface region at low annealing temperatures.^{3,7–13} A knowledge of the microstructure of such intermediate layers is, therefore, imperative to the understanding of the formation of the crystalline silicide and its associated properties. Hence we have investigated the structural changes associated with the zirconium/silicon system at relatively low annealing temperatures using extended x-rayabsorption fine-structure (EXAFS) measurements. Since EXAFS probes the short-range order of materials to ~ 5 Å from the atom of interest, it is sensitive to both amorphous and crystalline structures and, therefore, is a useful technique for investigating disorder-order structural transitions.

II. SAMPLE PREPARATION AND CHARACTERIZATION

Thin films (100 Å) of zirconium (99.8% pure) were electron-beam evaporated in UHV ($10^{-9}-10^{-10}$ Torr) onto 25.4 mm diameter *n*-type single-crystal Si(111) wafers. The silicon had previously been subject to UV/ozone irradiation to remove hydrocarbons and spun with an HF/alcohol mixture to remove the native oxide. The wafers were then immediately inserted into vacuum and further cleaned by heating to 900 °C for 10 min. The resulting surfaces exhibited a 7×7 Si(111) reconstructed low-energy electron-diffraction (LEED) pattern. The ambient temperature 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 425 °C.

In situ LEED and AES were performed on all samples after annealing. No oxygen contamination is evident from any of the AES plots. Figure 1 plots the ratio of the 147 eV zirconium AES peak and the 92 eV peak (containing contributions from both zirconium and silicon) as a function of annealing temperature. The decrease in amplitude of the zirconium peaks for any annealing temperature above ambient is indicative of an initial interdiffusion. The sudden and almost complete disappearance of the zirconium peaks in the region 350–375 °C indicates that some major structural rearrangement takes place at this temperature and silicon atoms start to appear at the surface of the film. This transition is most likely indicative of the onset of nucleation. In this temperature range, LEED results do not show the reemer-

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FIG. 1. The ratio of the 147 eV (Zr) Auger electron spectroscopy peak and the 92 eV (Si and Zr) peak vs annealing temperature. The sudden and almost complete disappearance of the zirconium contribution in the region 350-375 °C indicates that some major structural rearrangement has taken place.

gence of a 7×7 pattern (which would have indicated silicide islanding resulting in reexposure of the clean crystalline substrate over a large enough range to show reconstruction), nor any other pattern. Scanning electron microscopy performed before and after the transition temperature (viz. 300 and 400 °C) did not indicate any macroscopic differences and neither of the samples were islanded.

III. EXAFS EXPERIMENTS AND DATA ANALYSIS

X-ray absorption experiments on the Zr K edge (17 998 eV) were performed on beamline X-11A at the National Synchrotron Light Source with an electron-beam energy of 2.53 GeV and stored currents between 110 and 210 mA. The x-ray energy was defined by a double-crystal monochromator with Si(111) crystals. Harmonics were rejected by detuning the monochromator crystals with respect to one another, resulting in a decrease of 30% in the incident x-ray intensity. The energy calibration was monitored periodically with a transmission scan of a zirconium foil. The incident intensity was monitored by an ionization chamber containing a 3:1 ratio of argon to nitrogen.

Since x rays could not be transmitted through the silicon wafer, data were collected using low-angle total electron yield (TEY) detection^{14,15} at room temperature. The TEY technique was used instead of the fluorescence technique to reduce the effect of x-ray-diffraction peaks coming from the silicon substrate that could contaminate the EXAFS data. A potential difference of 300 V was applied between the sample and collecting plate which were separated by approximately 2 cm. The sample chamber was kept under a continuous flow of helium gas to enhance the signal by ionization. Edge steps (i.e., the magnitude of the change in the electron yield signal around the zirconium K-edge energy) of 0.2-1.6 were typically observed. The samples could be tilted or rotated with respect to the beam to maximize the signal and to try to minimize Bragg reflections from the crystalline substrate. Angles of $3^{\circ}-4^{\circ}$ from horizontal were routinely used. Multiple scans at different orientations were taken to help to identify the positions of Bragg peaks. Linearity checks between the incident signal and the total electron yield signal were performed and exhibited less than a 0.5% difference. Reference spectra of a zirconium foil were taken in both electron yield and transmission modes for comparison. About a 25% reduction in amplitude was apparent for the first shell electron yield data, probably due to the effect of the surface oxide which will be more dominant using the more surface sensitive electron yield technique. While this discrepancy should be held in mind, it does not detract from the general trend of the electron yield data, which is mainly what we will be concerned with here.

Pre- and postedge backgrounds were removed by fitting smooth, low-order polynomials to the appropriate regions of the experimental spectra using the Eindhoven routines.¹⁶ 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 non-linear least-squares fitting of the theoretical EXAFS function (χ) to the experimental data using the rapid curved wave theory of EXAFS¹⁷ as implemented in the program EXCURV88.¹⁸ As an illustration of the information available from EXAFS, we show a much simplified version of the EXAFS function below:

$$\chi(\kappa) = -\sum_{i=1}^{n} \frac{N_i A F A C}{\kappa R_i^2} \sin(2\kappa R_i + 2\delta + \psi_i) |F_i(\pi, \kappa)|$$
$$\times \exp(-A_i \kappa^2) \exp\left(\frac{-2R_i}{\lambda}\right).$$

Here κ is the photoelectron wave vector and N_i the number of neighboring atoms of type i in a shell of radius R_i having an electron-backscattering amplitude of $F_i(\pi,\kappa)$. The term A_i is a Debye-Waller factor giving a measure of the static and thermal disorder present in the system and is defined by $A_i = 2(\sigma_i)^2$, where σ_i is the rms deviation in the interatomic distances R_i . The sine term accounts for phase shifts experienced by the photoelectrons on their passage through the potentials of the emitting and scattering atoms. The phase shifts and backscattering factors for the zirconium and silicon atoms were theoretically generated by the program. The phase shifts were then empirically modified by fitting to the standard compound ZrSi₂ so that the structural parameters agreed, to within experimental error, with the accepted values. Transferability of these phase shifts was then tested by using them to fit to experimentally obtained spectra of other standards of known structure, namely zirconium metal, crystalline silicon,¹⁹ and zirconium silicate ($ZrSiO_4$).

The amplitude factor (AFAC) is used to account for absorption events that do not result in EXAFS (such as multielectron excitations) and was set at 0.8—the value obtained from the best fit to the zirconium metal data, since this term depends only on the absorbing atom. The elastic mean free path of the photoelectron is given by λ . This photoelectron mean free path (described in the program in terms of an imaginary part of the potential representing the photoelectron



FIG. 2. Results of fitting the zirconium near-edge data for 100 Å Zr on Si(111) with a linear combination of the data collected from an as-deposited sample and a sample annealed at 950 °C. The dominant structural rearrangement appears to take place at around 350-375 °C.

lifetime) was allowed to float around the value obtained for the $ZrSi_2$ standard sample, i.e., -8 eV, a typical value for such a metal-containing system.

Analysis of the experimental EXAFS data using multiparameter fitting in κ space, therefore, yields values for R, N, A, and a nonstructural parameter E_0 , which is used in the fitting routine to correct for the energy offset of the photoelectron at zero wave vector. The limit of significance of correlated parameters was calculated statistically within the EXCURV88 program²⁰ 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 error estimates derived from such contour plots that are quoted in this paper.

IV. RESULTS

The results from fitting the zironcium x-ray-absorption near-edge structure (XANES) with a linear combination of the data collected from the as-deposited sample (representing the initial phase of the reaction) and a sample annealed at 950 °C (which exhibits the final phase C49 ZrSi₂ structure²¹) are shown in Fig. 2. Since the features of the XANES spectra at the zirconium edge alter subtly rather than drastically, this linear combination fitting can be used to yield semiquantitative information about the temperature of any phase changes. The fact that, in the annealing temperature range investigated, the plot only ranges from around 30%-70% of the as-deposited spectrum is indicative of the fact that some reaction has already taken place at 300 °C and the ZrSi₂-like structure has not been obtained by 425 °C. However, the dominant structural rearrangement in this range appears to take place at around 350-375 °C, consistent with the Auger results of Fig. 1.

The κ^2 weighted zirconium K-edge EXAFS spectra are shown in Fig. 3. Even by eye one can see that the asdeposited sample bears close resemblance to the metallic foil



FIG. 3. The κ^2 -weighted zirconium K-edge experimental EXAFS spectra of 100 Å Zr on Si(111). There is a significant change in the spectra between annealing temperatures of 350 and 400 °C, but even at 425 °C the spectrum is not like that of crystalline ZrSi₂. The data are offset for clarity.

(also taken in e-yield), indicating essentially no reaction on deposition. After the annealing temperature of 300 °C, the data has a lower amplitude and a different phase, revealing some initial reaction. The amplitude of the data is increased in the 350 °C annealed sample. The 400 °C annealed sample has taken on a significantly different form which is further enhanced in the 425 °C data. It should be noted that this is the same temperature region where significant structural rearrangement was indicated by AES and fitting of the XANES data. Also, even at the highest temperature reported here, the EXAFS data does not yet indicate a $ZrSi_2$ -like structure, which is shown for comparison. A typical κ -space fit is shown in Fig. 4.

The κ^2 -weighted Fourier transforms of the EXAFS data taken over the κ -space range 3–10 Å⁻¹ are shown in Fig. 5. The plots were generated with a Hanning window value of 0.1. These spectra readily indicate the increasing order with increasing annealing temperature and the evolution of higher shells can clearly be seen.

The EXAFS fitting results are presented in Table I. The energy offset (E_0) was allowed to float during the fitting and increased from 2.4 to 9.4 (±1.3) eV with increasing annealing temperature. The results indicate a first shell (Zr-Si) distance similar to that for ZrSi₂ (2.81 Å) for all annealing temperatures above and including 350 °C, but the sample annealed at 300 °C shows a slightly larger distance (though this may be due to an increased error resulting from the low signal-to-noise ratio of this data) and a large Debye–Waller factor indicative of significant disorder. While the errors quoted for the higher shell Debye–Waller factors and coordination numbers are large, the parameter values are still displayed in the table to indicate the trends of the data. All



FIG. 4. A typical κ -space fit of the EXAFS data of 100 Å Zr on Si(111) annealed at 400 °C.

samples show a reduced coordination with respect to ZrSi₂ where the first shell coordination number is 10. Increased coordination is induced with progressively higher annealing temperatures, but even at 425 °C, a C-49-like structure has not formed. Indeed, for the higher annealing temperature samples presented here, the second peak (Zr-Zr) seems to be split into two approximately equal subshells (at distances around 3.4 and 3.8 Å) with a total coordination of around 12 for the highest annealing temperature (425 °C). None of the first shell fitting distances are consistent with the first Zr-Zr distances in metallic zirconium (around 3.20 Å), indicating that no unreacted metal is being seen. Indeed, the fitting results of the higher temperature data was found to be in close agreement with the atomic distribution of crystalline ZrSi (generated using a crystal modeling program, ISTRUC). The data for both ZrSi and ZrSi₂ are shown in Table I for comparison. For these theoretical results, the shell information is presented as the average of like shells that are closer than 0.25 $Å^{22}$ and the Debye–Waller factor (A) was calculated from the spread of interatomic distances of these subshells.



FIG. 5. The κ^2 -weighted Fourier transforms of the EXAFS data shown in Fig. 3, taken over the κ -space range 3-10 Å⁻¹ with a Hanning window of 0.1. Increasing ordering and the evolution of higher shells can easily be seen as the annealing temperature is increased. The data are offset for clarity.

V. DISCUSSION

EXAFS, AES, and XANES fitting all indicate some initial reaction of zirconium and silicon at 300 °C, though none indicate any significant interdiffusion in the as-deposited sample at the levels detectable by these techniques. The EXAFS analysis shows the resulting layer to be of a disordered-intermixed phase. Such an amorphous layer has been observed by others using cross-sectional transmission electron microscopy (TEM)¹¹⁻¹³ for zirconium on both Si(111) and Si(100) at annealing temperatures between 350 and 480 °C. However, these studies involve considerably thicker metal depositions (500-2000 Å) than reported here (100 Å), and metallic zirconium remains on the surface of the sample even as the interface reaction proceeds through initial steps. Since EXAFS reports the average structure around the atom of interest, our films were fabricated considerably thinner to observe the interaction at the interface without interference from the presence of the metallic phase. Indeed, no evidence of metallic zirconium is seen in any of

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

Anneal temp.	R _{Zr-Si} (Å)±0.01	N _{Zr-Si} ±1.0	A_{Zr-Si} (Å ²)±0.005	$\begin{array}{c} R_{\text{Zr-Zr}} \\ \text{(Å)} \pm 0.02 \end{array}$	N _{Zr-Zr} ±2.0	A_{Zr-Zr} (Å ²)±0.01	R _{Zr-Zr} (Å)±0.04	N _{Zr-Zr} ±3.0	A _{Zr-Zr} (Ų)±0.015
300 °C	2.92	2.8	0.014	•••		•••	•••		•••
350 °C	2.83	2.9	0.001	3.38	2.0	0.013	3.88	0.7	0.006
400 °C	2.82	5.2	0.007	3.37	2.6	0.004	3.82	2.4	0.007
425 °C	2.82	7.7	0.013	3.39	6.1	0.011	3.79	6.1	0.013
ZrSi	2.78	7.0	0.005	3.40	6.0	0.0001	3.76	4.0	0.001
ZrSi ₂	2.81	10	0.017	3.64	6.0	0.015	4.68 Zr-Si	12 Si	0.001 Zr-Si

the spectra indicating that even at 300 °C, all of the zirconium has interacted with the substrate. However, for the thicker films investigated by Yamauchi *et al.*,¹³ the metallic phase remained for annealing temperatures as high as 460 °C.

Above 350 °C the film starts to undergo significant structural changes and the majority of this rearrangement is completed by 375 °C, as indicated by AES and XANES fitting. In the EXAFS analysis, the stability of the first- and second-nearest-neighbor distances in the range 350-425 °C imply that the first ordered state nucleates at around 350 °C. With increasing temperature, the coordination of these nearest-neighbor shells increases and the structure becomes considerably more ordered. By 425 °C the interface region has assumed a ZrSi-like structure, rather than the C49 ZrSi₂ structure that is formed at higher annealing temperatures (around 700 °C).²¹ This is consistent with the results of Chen¹⁰⁻¹² who observed small grains of ZrSi by crosssectional TEM after annealing 300 Å zirconium films to 550 °C for 1 h or 500 Å films to 480 °C for 1.5 h. As expected, for our thinner films prepared in UHV, the nucleation of the crystalline ZrSi phase begins at a lower temperature (350 °C), even with a relatively short annealing time.

However, Yamauchi *et al.*,¹³ while observing an amorphous silicide interlayer on annealing 400–2000 Å Zr/Si (100) films above 420 °C for 30 min, did not observe any other crystalline phase except ZrSi_2 , which started to nucleate at around 400 °C. Apart from the obvious differences in film thickness and substrate between our work and theirs, Yamauchi *et al.*¹³ also reported that their initial metallic film was amorphous, which ours is not.

Cheng and Chen¹² further reported that the observed crystalline ZrSi formed at the crystalline silicon–amorphous interlayer interface, but there was no evidence of ZrSi at the metal–amorphous interlayer interface. This would agree with our observation of the formation of ZrSi where no metal phase was present at the onset of nucleation.

The formation of a disordered-intermixed layer, as described here for the 300 °C annealing temperature, is generally attributed to the anomalously fast diffusion of one element in the other at low temperatures. In the zirconium/ silicon system, silicon is the dominant diffusing species and the formation of the disordered layer is predominantly driven by a negative free energy of mixing.¹² The fast random diffusion of silicon atoms in zirconium can result in atomic arrangements significantly different from the first stable crystalline phase and these disordered-intermixed regions thus possess considerable local strain. Hence the free energy of the system can be described in a three-dimensional diagram as shown in Fig. 6.23 Here, A represents the as-deposited state, while C represents the first stable silicide, i.e., ZrSi. The degree of intermixing is dependent on the diffusion rate and temperature, but for the conditions outlined above the reaction path may proceed towards state D, representing a metastable disordered-intermixed phase with a composition similar to the crystalline phase C. However, the disordered state is considerably strained and at some point along the pathway A-D nucleation may be triggered, leading directly to the lower free energy of the crystalline state. The nucle-



FIG. 6. Free-energy diagram in terms of intermixing and strain of a metal/ silicon film. A represents the as-deposited state, B the nucleation point, C the first stable silicide, i.e., ZrSi, and D a metastable disordered-intermixed phase with a composition similar to C.

ation point is represented by *B*. In our zirconium/silicon samples, this nucleation point appears to be at around 350 °C with the crystalline ZrSi phase being only just formed at ~425 °C.

VI. CONCLUSIONS

We have reported EXAFS results on 100 Å films of zirconium deposited on Si(111) and annealed to moderate temperatures (300-425 °C). The EXAFS fitting results suggest that a ZrSi crystalline phase evolves from a disorderedintermixed phase as a precursor to the $ZrSi_2$ C49 phase in this system. A possible mechanism for this procedure was discussed in terms of free energy, interdiffusion, and the resulting strain of the disordered-intermixed layer. However, the exact reaction path is dependent on criteria such as film thickness and annealing time. The effects of these parameters are currently under investigation using x-ray-absorption spectroscopy and other techniques.

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