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EXAFS Study of the Initial Interface Region Formed by Thin Zirconium and Titanium Films on Silicon(111)

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While titanium has long been of interest for use in creating low resistivity metal contacts on silicon, the commonly resulting epitaxial silicide ($TiSi_2$) is often of C49 phase and is, unfortunately, metastable - transforming to the stable C54 phase at higher temperatures. Zirconium, however, only exhibits a C49 phase disilicide and, being in the same periodic group, is chemically similar to Ti, affording the possibility of alloying small quantities of Zr with Ti in order to stabilize the epitaxial C49 structure. Both Ti and Zr have been reported to show a strongly disordered interface region at low temperatures, but little quantitative structural work has been performed on the Zr:Si system. To this end, an initial structural study of the Zr on Si (111) system has been undertaken. Thin films (100Å) of Zr were deposited in UHV conditions onto atomically clean Si(111) wafers and annealed in situ at fine temperature intervals between 300 and 425°C, over which range Auger spectroscopy indicated Si diffusion to the surface. A comparison will be made with the Ti:Si system for samples of 100Å Ti prepared under the same conditions.

Keywords: EXAFS, Interface, Zirconium Silicide, Titanium Silicide.

1. 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. While the thrust of work to date has concentrated on titanium, which forms the lowest resistivity contact, the commonly resulting epitaxial silicide ($TiSi_2$) is often of C49 phase and is, unfortunately, metastable - transforming to the stable C54 phase at high temperatures [1]. Zirconium, however, only exhibits a C49 phase disilicide, affording the possibility of alloying small quantities of Zr with Ti in order to stabilize the epitaxial C49 structure at all temperatures.

2. SAMPLE PREPARATION

In order to investigate the interaction of the zirconium/silicon system, 100Å Zr films were e-beam evaporated in UHV (10^{-9} - 10^{-10} Torr) onto atomically clean, single-crystal Si(111) at ambient temperature. These samples were then annealed in situ at temperatures between 300 and 425°C for 20 minutes.

In situ Auger electron spectroscopy (AES) was performed on all samples after annealing. The decrease in amplitude of the Zr peaks for any annealing temperature above ambient is indicative of an initial interdiffusion. The sudden and almost complete disappearance of the Zr peaks at around 350°C indicates that some major structural rearrangement takes place at this temperature and Si atoms start to appear at the surface of the film.

To make a meaningful comparison with the titanium/silicon system, 100Å Ti films were deposited onto Si(111) under identical conditions. AES indicated a rapid reduction in the amplitude of the Ti peaks at around 425°C, and hence the Ti samples were annealed for 20 minutes at temperatures between 300 and 475°C.

3. EXPERIMENTAL

X-ray absorption experiments on the Zr K-edge (17998 eV) and Ti K-edge (4966 eV) were performed on beamline X11A of the NSLS with an electron beam energy of either 2.53 or 2.58 GeV and stored currents 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 the appropriate metallic foil. Harmonics were rejected by detuning the crystals 30% for Zr and 60% for Ti. Data were collected using low-angle total electron yield detection [2] at room temperature and edge jumps of 0.2 to 1.6 were typical. The samples could be tilted or rotated with respect to the beam to try to minimize Bragg reflections.

4. RESULTS

Only preliminary data analysis has been performed. The data were background subtracted using the Eindhoven routines and structural information was obtained using the EXCURV88 curved wave package [3]. The theoretically generated phase shifts were empirically modified by fitting to the standard compounds of $ZrSi_2$ and $TiSi_2$ [C54 phase] so that their structural parameters agreed, to within experimental error, with their accepted values.

The amplitude factor was set at 0.8 for both the Zr and Ti data. The photoelectron mean free path, described in terms of an imaginary part of the potential in the fits, was allowed to float around the values obtained for the standard samples.

The k^2-weighted Zr K-edge EXAFS spectra are shown in Fig. 1. Major diffraction peaks from the crystalline substrate have been removed, but the usable data range is short, especially for the lower annealing temperature samples. However, even by eye one can see that the as-deposited sample bears close agreement to the metallic foil (also taken in e-yield). After the annealing temperature of 300°C, the data has a lower amplitude and a different phase, indicating some initial reaction. The amplitude of the data is increased in the 350°C annealed sample, but after 400°C it takes 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 some major structural rearrangement was indicated by AES. Also, even at the highest temperature, the EXAFS data does not yet indicate a $ZrSi_2$-like structure.

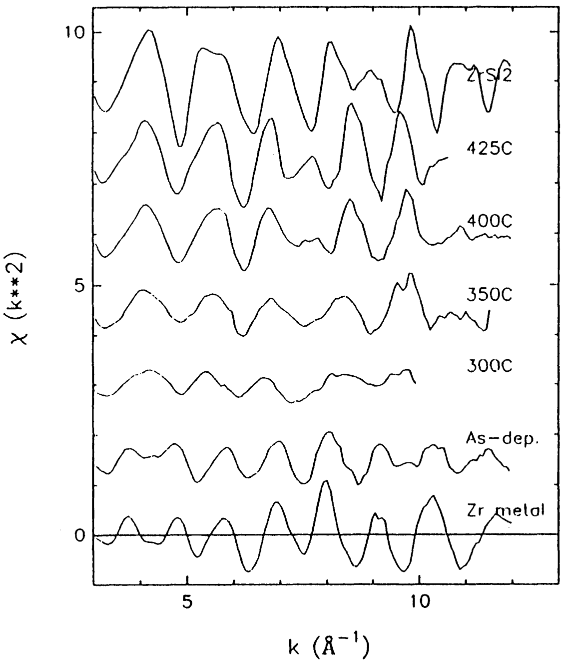

Figure 1. k^2-weighted Zr K-edge EXAFS spectra.

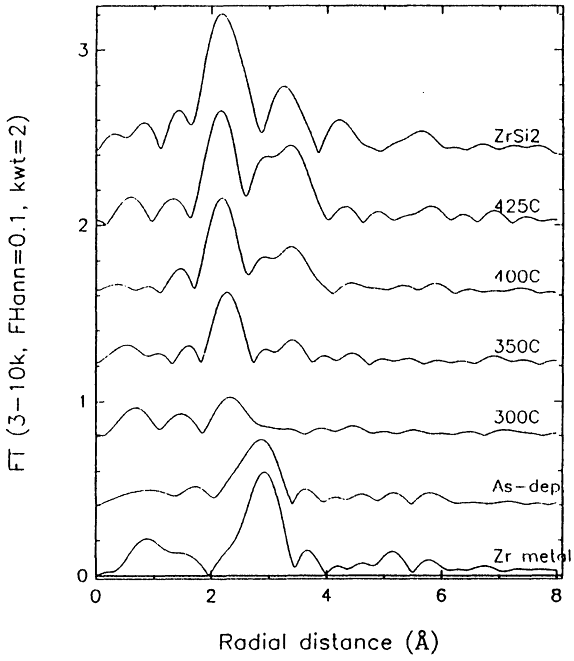

Figure 2. k^2-weighted Fourier transforms of the Zr K-edge data taken over the range 3 - 10 $Å^{-1}$.

The k^2-weighted Fourier transforms of the EXAFS data taken over the range 3-10 $Å^{-1}$ are shown in Fig. 2. These more readily indicate the increasing order with increasing annealing temperature and the evolution of higher shells can clearly be seen.

The preliminary EXAFS fitting results are presented in Table I. The energy offset (E0) was allowed to float during the fitting and increased from 2.4 to 9.4 eV with increasing annealing temperature. The results indicate a first shell (Zr-Si) distance similar to that for $ZrSi_2$ (2.81Å) 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. All samples show a reduced coordination with respect to $ZrSi_2$ where the first shell coordination number is 10. Ordering is induced with progressively higher annealing temperatures, but even at 425°C, a C49-like structure has not formed. Indeed, for the higher annealing temperature samples, 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 13 for the highest annealing temperature, whereas $ZrSi_2$ has a second shell of 6 Zr atoms at 3.64Å and a third shell of 12 Si atoms at 4.68Å. Neither are these fitting distances consistent with the first Zr-Zr distances in metallic Zr (around 3.20Å) indicating that no unreacted metal is being seen. The fitting results were compared to the atomic distributions of other known Zr:Si crystalline structures (ZrSi, Zr_5Si_4, Zr_5Si_3 and Zr_2Si) generated using the ISTRUC program and the higher temperature data was found to be in close agreement with that of ZrSi, the theoretical results for which are also shown in Table I. This suggests that the ZrSi crystalline phase evolves from the disorder as a precursor to the $ZrSi_2$ C49 phase. This is consistent with the results of Cheng [4]) who reported small (50Å) grains of ZrSi by TEM, after annealing 300Å films of Zr on Si at 500°C.

The k^2 Ti K-edge EXAFS spectra are shown in Fig. 3 and the k^2-weighted Fourier transforms in Fig. 4. In this case, 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 2.88Å), but with reduced coordination (3.8 and 4.1 respectively, as opposed to 6 for the metal). The samples annealed at 425 and 475°C are extremely like the C49 phase (which has 10 Si atoms at around 2.70Å and 6 Zr atoms at around 3.51Å). The coordination numbers in the first shell (Ti-Si) of the annealed samples are close to the theoretical value, but those in the second shell (Ti-Ti) are reduced. The similarities between the structures of the annealed samples and those of the metal or C49 phase is further evidenced by the XANES structure. Fitting the XANES data with a linear combination of the as-deposited and 475°C data supports these conclusions and indicates the 400°C annealed sample to be an almost equal mix of the two end points. However, least-squares fitting of the EXAFS data returned first shell parameters of 6.1 Si atoms at 2.63Å, which is in close agreement with the theoretically generated parameters for TiSi [BFe structure] (7 Si atoms at 2.63Å). A more detailed analysis is required to obtain second shell data before this conclusion can be confirmed.

Table I. Results of preliminary fitting to Zr K-edge data.

Anneal. Temp.	$R_{Zr\text{-}Si}$ (Å)	$N_{Zr\text{-}Si}$	$\sigma^2_{Zr\text{-}Si}$ (Å^2)	$R_{Zr\text{-}Zr}$ (Å)	$N_{Zr\text{-}Zr}$	$\sigma^2_{Zr\text{-}Zr}$ (Å^2)	$R_{Zr\text{-}Zr}$ (Å)	$N_{Zr\text{-}Zr}$	$\sigma^2_{Zr\text{-}Zr}$ (Å^2)
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	----	3.40	6.0	----	3.76	4.0	----

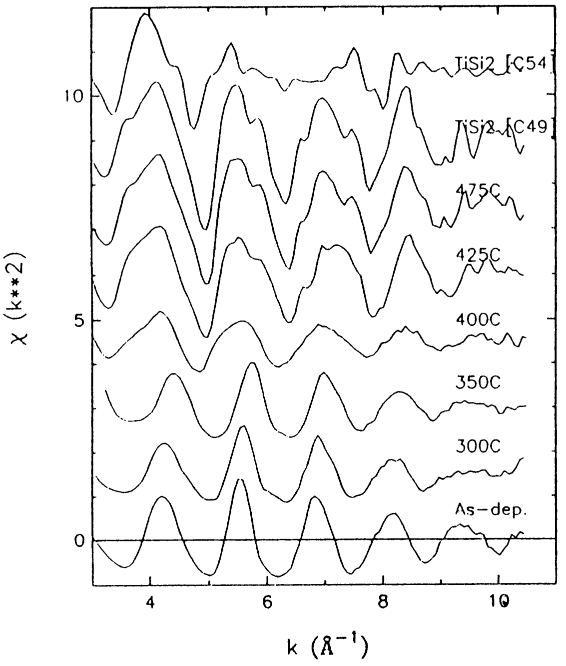

Figure 3. k^2-weighted Ti K-edge EXAFS spectra.

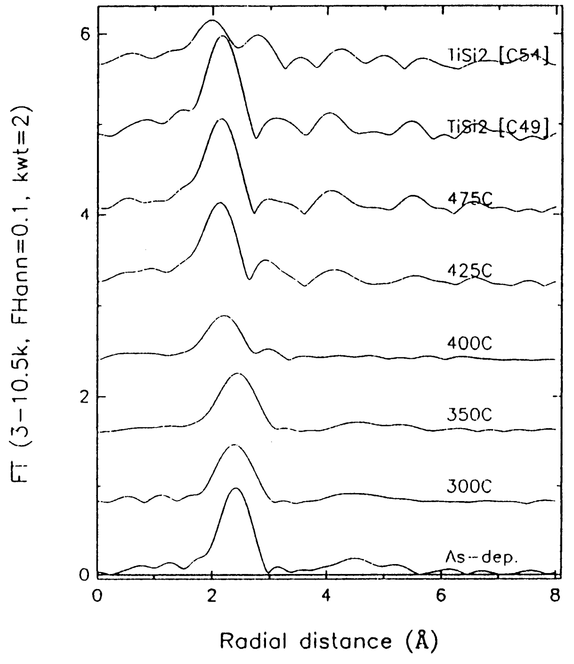

Figure 4. k^2-weighted Fourier transforms of the Ti K-edge data taken over the range 3 - 10.5 Å^{-1}.

5. CONCLUSIONS

A preliminary analysis has been made of the initial structural changes induced at the interface of Zr/Si (111) and Ti/Si (111) with increasing annealing temperatures between 300 and 475°C. The Zr data indicates some initial reaction of Zr and Si even at 300°C, resulting in a disordered-intermixed phase. At 350°C the structure is becoming more ordered, and by 425°C the interface region has assumed a ZrSi-like structure, rather than the $ZrSi_2$ structure that is formed at higher annealing temperatures $^{5)}$.

In contrast, the Ti film shows little reaction with the silicon substrate until above 350°C. At 400°C there is evidence of an intermixed phase that may be TiSi [BFe structure]. By 425°C the C49 phase $TiSi_2$ structure has already nucleated indicating that the reaction sequence occurs much faster and at a lower temperature for Ti than for Zr, although it is not initiated until a higher temperature than for Zr.

In conclusion, Zr and Ti appear to follow similar structural reaction paths when annealed on Si (111) and this suggests that alloying small amounts of Zr with Ti to stabilize the C49 structure would be possible. However, there is some difference in the kinetics of these reactions and thus this procedure may result in some form of phase separation.

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