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Local structural studies of $(Ti_{1-x}Zr_x)Si_2$ thin films on Si(1 1 1)

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Abstract

$Ti_{1-x}Zr_x$ ($0 \leqslant x \leqslant 0.2$) films were prepared by co-deposition onto Si(1 1 1) surfaces in UHV. After in situ thermal annealing at temperatures of ~ 600°C, the films form C49 $(Ti_{1-x}Zr_x)Si_2$ and are stable in this phase up to at least 910°C. A quantitative X-ray absorption spectroscopy analysis was performed to study the local structure of these alloy films. The structure of the C49 alloy silicide is more ordered in the perpendicular direction to the sample surface than the parallel direction. The Zr–Si bond lengths are shorter compared to the $ZrSi_2$ films.

$TiSi_2$ exhibits two different phases, a metastable C49 phase with an orthorhombic base centered structure and a stable C54 phase with an orthorhombic face centered structure. Previous studies have shown that Si diffuses into the Ti and reacts initially to form the C49 $TiSi_2$ phase at about 450°C. After annealing at higher temperatures (> 700°C), the $TiSi_2$ transforms to the stable C54 phase [1].

However, accompanying the C54 phase transition is the tendency towards agglomeration at high temperatures (> 700°C). This effect can significantly degrade the sheet resistance of the C54 phase of $TiSi_2$ films less than 400 Å thick [2, 3]. Meanwhile, $ZrSi_2$ has only a stable C49 phase. Our recent work showed that the C49 phase of $TiSi_2$ can be stabilized at higher annealing temperatures (600–910°C) by alloying the Ti with a small percentage of Zr [4]. The alloy silicide films at high temperatures have a smoother surface than the $TiSi_2$ films. After annealing at higher temperatures (> 600°C), the sheet resistivity of the C49 alloy films is much lower than the $TiSi_2$ C49 films at about 600°C.

Ti and Zr atoms were co-deposited on the atomically cleaned Si(1 1 1) substrates by electron beam evaporation at room temperature in UHV ($\sim 5 \times 10^{-10}$ Torr). The total thickness of the alloy films was 200 Å. The samples were annealed in situ at temperatures between 600 and 910°C for 20 min.

In order to understand the structural properties of the C49 alloy films, an XAFS analysis was performed to study $(Ti_{1-x}Zr_x)Si_2$ films on Si. The XAFS experiments were carried out on beamline X-11A of the NSLS as described elsewhere [5]. To examine the local atomic structure around Ti and Zr, Ti K-edge and Zr K-edge EXAFS experiments were performed. To examine crystal orientation effects, data were collected with the sample surface oriented both parallel and perpendicular to the polarization of the incident X-rays.

Fig. 1 shows the Fourier transforms of the k^3-weighted Ti K-edge EXAFS of the standard $TiSi_2$ film (sample A) and the C49 $(Ti_{0.9}Zr_{0.1})Si_2$ film (sample B). The data were analyzed using the University Washington package. Fitting was performed using FEFF. The fitting results are shown in Table 1.

As shown in Fig. 1, the Ti–Si peak amplitude is greater in the perpendicular direction to the sample surface than in the parallel direction for the C49 $(Ti_{0.9}Zr_{0.1})Si_2$ film. The Ti–Si peak amplitude for the standard $TiSi_2$ film annealed at 600°C is smaller than the alloy sample annealed at 810°C. Fitting results suggest that the Debye–Waller (DW) factor of the C49 $TiSi_2$ film is larger than

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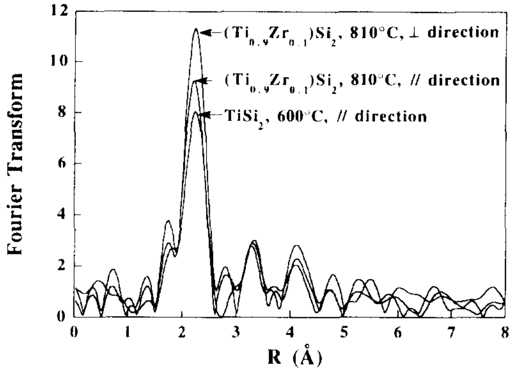

Fig. 1. Fourier transforms of the k^3-weighted Ti K-edge EXAFS from 2.85 to 12.15 Å^{-1} of C49 $TiSi_2$ and $(Ti_{0.9}Zr_{0.1})Si_2$.

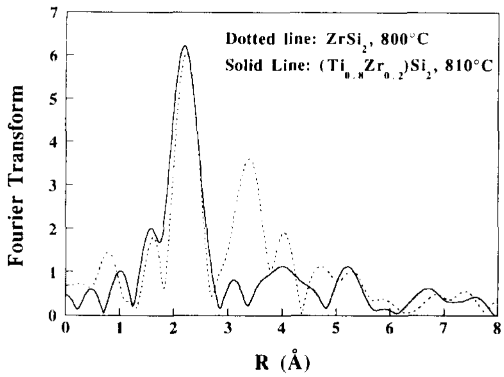

Fig. 2. Fourier transforms of the k^3-weighted Zr K-edge EXAFS from 2.75 to 10.5 Å^{-1} of C49 $ZrSi_2$ and $(Ti_{0.8}Zr_{0.2})Si_2$.

Table 1
Fitting results for $TiSi_2$, $ZrSi_2$, and $(Ti_{1-x}Zr_x)Si_2$ films

Sample	R_{Ti-Si} (Å)	N	DW(10^{-4})
Fitting results of Ti K-edge EXAFS data			
A, ∥ direction	2.61 ± 0.01	6.5 ± 0.5	64 ± 5
B, ∥ direction	2.61 ± 0.01	6.7 ± 0.5	50 ± 5
B, ⊥ direction	2.61 ± 0.01	6.7 ± 0.5	34 ± 5

Sample	Ave. R_{Zr-Si} (Å)	R_{Zr-Si} (Å)	N	DW(10^{-4})
Fitting results of Zr K-edge EXAFS data				
C	2.80 ± 0.01	2.74 ± 0.01	6.0 ± 0.05	4 ± 5
		2.88 ± 0.01	4.0 ± 0.5	1 ± 5
D	2.74 ± 0.01	2.68 ± 0.01	6.0 ± 0.5	17 ± 5
		2.82 ± 0.01	4.0 ± 0.5	6 ± 5

that of the C49 $(Ti_{0.9}Zr_{0.1})Si_2$ film. The DW factor is smaller in the perpendicular direction than in the parallel direction for the C49 $(Ti_{0.9}Zr_{0.1})Si_2$ film.

The Fourier transforms of Zr K-edge k^3-weighted EXAFS of the standard C49 $ZrSi_2$ film (800°C) (sample C) and the C49 $(Ti_{0.8}Zr_{0.2})Si_2$ film (810°C) (sample D) are shown in Fig. 2. Ten nearest Si atoms around the central Zr atom were modeled to have two unequivalent positions. For the best fit, six of the Si atoms are surrounded by six Zr atoms in a plane and four are at the center of four Zr in a tetragonal arrangement. The weighted average Zr–Si bond lengths were calculated. The fitting results are also summarized in Table 1. As shown in Table 1, the C49 $(Ti_{0.8}Zr_{0.2})Si_2$ has a smaller average Zr–Si bond length compared to the standard $ZrSi_2$.

In conclusion, the Zr–Si bond lengths in the C49 alloy films are shorter compared to the standard $ZrSi_2$ film. The alloy C49 alloy films annealed at high temperatures (~ 810°C) are more ordered than the C49 $TiSi_2$ films (~ 600°C). In addition, the C49 alloy films are more ordered in the perpendicular direction to the sample surface than in the parallel direction.

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