# X-ray Absorption Study of the Reaction of Zirconium Thin Films on Silicon(111)

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# X-ray Absorption Study of the Reaction of Zirconium Thin Films on Silicon(111)

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X-ray absorption measurements of 100Å Zr thin films deposited on Si(111) substrates in UHV have been obtained by using a total electron yield detector. Experiments were performed on Zr/Si thin films in order to obtain structural information and find the optimum annealing temperature to produce uniform $ZrSi_2$ epitaxial thin films on Si(111) substrates. A quantitative X-ray absorption fine structure analysis indicates that the films annealed above 650°C form $ZiSi_2$ disilicides, which have the orthorhombic-base centered C49 structure.

KEYWORDS: EXAFS, XANES, total electron yield, thin film, $ZrSi_2$, silicides.

## 1. INTRODUCTION

Refractory metal silicides are important materials for application in Very Large Scale Integrated circuits (VLSI) as contacts, electrodes and interconnects, which require high temperature stability, low resistivity and compatibility with current processing steps [1, 2]. Among refractory metal silicides, $TiSi_2$ is considered to be the optimal choice, because of its lowest contact resistivity and highest thermal stability in group IVb [3]. However, very little work has been done on Zr/Si system. Zr is in IVb group as Ti and it silicides also possess excellent electrical and thermal properties as the contact material [4].

It is well known that $TiSi_2$ has both a metastable C49 phase, which has a lower surface free energy, and a stable C54 phase, which has a lower bulk free energy. However, $ZrSi_2$ has only a stable C49 structure. This should provide a smoother surface than the C54 structure. The resistivity of Zr disilicide is 35~40 μΩ·cm, which is higher than that of $TiSi_2$, but a little lower than that of Zr metal, which is as low as that of Ti metal. [4]

In this work, local structures and surface morphologies of Zr/Si films annealed at different temperatures are studied by AES, XANES and EXAFS techniques. An optimal annealing temperature range to form uniform $ZrSi_2$ films is found.

## 2. EXPERIMENTS

Films were prepared in a UHV chamber with a base pressure of $4 \times 10^{-10}$ Torr. The Si wafer cleaning procedure included precleaning by exposure to UV/ozone irradiation to remove hydrocarbon contamination from the surface, HF spinning etching to remove oxide from the surface, and heat cleaning to 850°C for 20 minutes in the UHV chamber to remove hydrogen and other residues. The LEED pattern of the cleaned substrates exhibited a 7x7 Si(111) reconstructed structure. In-situ AES showed no detectable carbon or oxygen. 100Å Zr films were deposited on the atomically cleaned Si(111) substrates by electron beam evaporation at room temperature. The thickness and the deposition rates were monitored by a quartz crystal oscillator. The samples were subsequently annealed at temperatures from 200°C to 950°C for 20 minutes in situ. In situ LEED patterns and AES spectra were taken after sample annealing.

The XAS experiments were carried out at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) on the X-11A beam line. The stored electron current was between 110 and 210 mA with a beam energy of 2.5 GeV. A double crystal monochromator with Si(111) crystals was used to select the photon energy of the incident beam. The angle of the monochromator crystal faces was adjusted to get rid of the high order harmonics by detuning the incident beam by 30% from its maximum. A copper foil was used to calibrate the photon energy. Data of the 100Å Zr/Si samples was collected by using the low angle total electron yield technique. The intensity of the incident x ray beam was measured by an ionization chamber, which was filled with argon and nitrogen at a fixed ratio. The intensity of the total electron current was measured by using a total electron yield detector with a helium gas flow. The sample and a collection plate were biased so that the ejected electrons outcoming from the sample were collected. A rotatable sample holder was used to minimize the Bragg peaks from the Si substrate. The angle of the sample surface and the incident x ray beam was also adjusted to be small to obtain a large footprint of the incident beam on the sample surface to enhance the signal to noise ratio. By adjusting this angle, we could also minimize Bragg peaks in the energy range in which we were interested.

## 3. RESULTS AND DISCUSSION

From standard Auger spectra tables, it is found that silicon has a single peak at the energy of 92 eV, and zirconium has peaks both at 92 eV and at 147 eV. The 147 eV peak represents the existence of Zr atoms and the 92 eV peak is a mixed signal of Si and Zr atoms. In the Auger spectrum of the as-deposited film, the magnitude of the 147 eV peak and that of the 92 eV peak are almost equal. This indicates that the as-deposited film is almost pure Zr metal. Zr atoms have limited reaction with the Si substate without annealing. A dramatic change takes place at annealing temperatures between 350°C and 375°C. The 92 eV peak starts to dominate. The magnitude of the 92 eV peak becomes much larger than that of the 147 eV peak. This indicates the exposure of the Si atoms on the surface of the film.

In-situ post-annealing LEED experiments showed no LEED pattern until annealed at 850°C. After being annealed at 850°C for 20 minutes, a 1x1 pattern was seen. The sample annealed at 900°C for the same amount of time gave a good 7x7 spot pattern. The LEED patterns follow the steps of nucleation, island formation in the Zr/Si layer, and finally, exposure of the Si substrate to the surface.

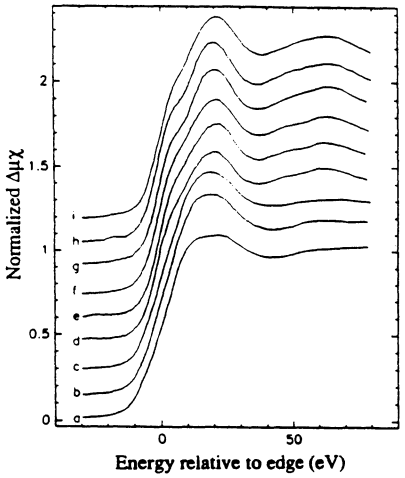


FIG. 1. The XANES structures of as-deposited Zr/Si film (a) and the films annealed at 200°C (b), 300°C (c), 400°C (d), 500°C (e), 600°C (f), 700°C (g), 800°C (h) and 950°C (i).

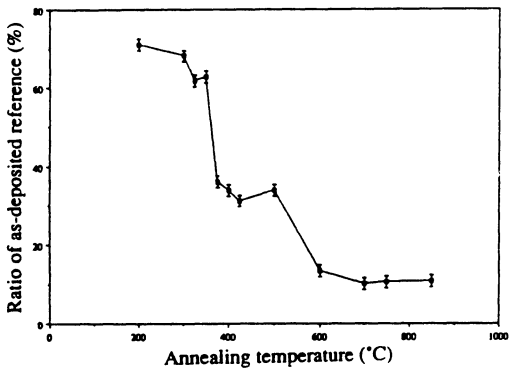


FIG. 2. Percentages of the as-deposited film reference on the XANES spectra at different annealing temperatures.

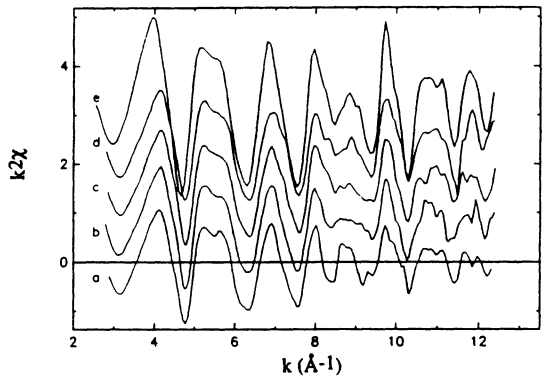


FIG. 3. $k^2$ weighted EXAFS oscillations of Zr/Si films annealed at 550°C (a), 650°C (b), 800°C (c), and 900°C (d), and $ZrSi_2$ powder sample (e).

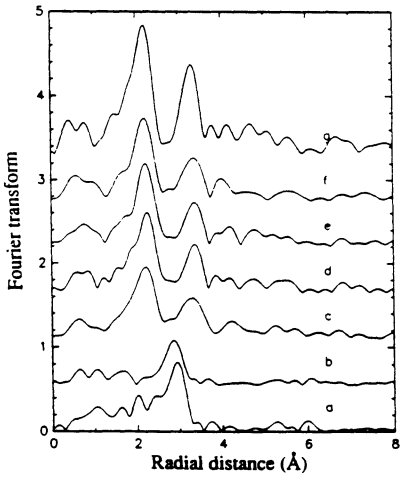


FIG. 4. $k^2$ weighted Fourier transforms of Zr foil (a), as-deposited Zr/Si film (b), Zr/Si films annealed at 550°C (c), 650°C (d), 800°C (e) and 900°C (f), and $ZrSi_2$ powder sample (g).

Figure 1 shows comparison of the x ray absorption near edge structures (XANES) of the films annealed at different temperatures. A shoulder starts to show up in the Zr absorption edge (17998 eV) at 400°C annealing, and the near edge feature gets more structure, compared to the 300°C annealed film. These changes become more and more pronounced as the annealing temperature goes up. If we use the XANES spectra of the as-deposited film and the film annealed at the highest temperature, 950°C, as two references to linearly fit spectra between 200°C and 950°C, the ratios of both of references are obtained. The results show very interesting features. The ratio of XANES spectra of the as-deposited film is shown in figure 2. As the annealing temperature increases the ratio of the as-deposited reference drops. Two distinct steps are visible. The first significant drop takes place between 350°C and 375°C. This indicates that the reaction between the Zr film and the Si substrate occurs at about 375°C annealing temperature. This is supported by the Auger results. The second dramatic drop takes place between 600°C and 700°C. This indicates another structural change at about 700°C.

Figure 3 shows the $k^2$ weighted EXAFS of the Zr/Si film annealed at 500°C, 650°C, 800°C and 900°C, as well as the standard $ZrSi_2$ powder, after pre-edge substraction of the raw data, normalization, background removal, and conversion from energy scale to wave vector, $k$. The Fourier transforms of these data, as well as the data of the as-deposited film and Zr foil over a k range of 2.9-13.4 $Å^{-1}$ are shown in figure 4. The features of the films annealed above 550°C are very similar to those of the C49 phase $ZrSi_2$ powder. Inverse Fourier transforms were performed over a range of 1.3 to 3.7 Å to isolate the first two shells. $ZrSi_2$ has the base-centered orthorhombic structure. Every Zr atom is surrounded by 10 nearest Si atoms and 6 nearest Zr atoms. Among the 10 Si atoms of the first shell, there are two unequivalent positions. Six are at an average distance about 2.73 Å, and each of them is surrounded by 6 Zr atoms in a plane. Four are at an average distance of 2.84 Å, and each of these is at the center of 4 Zr in a tetragonal arrangment. Using the curved-wave XAFS simulation program (FEFF),

TAB. 1. Fitting results of Fourier back transformations of first two nearest neighbour shells around a Zr atom.

| Zr/Si Sample | Shell | Bonding | N | R(Å) | $\sigma^2(10^{-4}$ Å $^2)$ |
|---|---|---|---|---|---|
| Zr Foil | 1 | Zr—Zr | 13.0 ± 0.2 | 3.20 ± 0.01 | 99 ± 9 |
| As-deposited | 1 | Zr—Zr | 11.0 ± 0.2 | 3.21 ± 0.01 | 125 ± 10 |
| 550°C | 1 | Zr—Si | 5.8 ± 0.2 | 2.73 ± 0.01 | 57 ± 3 |
| | 1 | Zr—Si | 3.2 ± 0.2 | 2.84 ± 0.01 | 102 ± 9 |
| | 2 | Zr—Zr | 1.4 ± 0.1 | 3.30 ± 0.01 | 41 ± 6 |
| | 2 | Zr—Zr | 6.8 ± 0.2 | 3.67 ± 0.01 | 70 ± 3 |
| 650°C | 1 | Zr—Si | 5.8 ± 0.1 | 2.74 ± 0.01 | 45 ± 2 |
| | 1 | Zr—Si | 3.6 ± 0.1 | 2.83 ± 0.01 | 78 ± 5 |
| | 2 | Zr—Zr | 0.2 ± 0.1 | 3.30 ± 0.01 | 8 ± 6 |
| | 2 | Zr—Zr | 6.6 ± 0.2 | 3.67 ± 0.01 | 60 ± 2 |
| 800°C | 1 | Zr—Si | 5.9 ± 0.1 | 2.73 ± 0.01 | 6 ± 3 |
| | 1 | Zr—Si | 3.9 ± 0.1 | 2.85 ± 0.01 | 5 ± 3 |
| | 2 | Zr—Zr | 6.4 ± 0.2 | 3.66 ± 0.01 | 59 ± 4 |
| 900°C | 1 | Zr—Si | 6.1 ± 0.1 | 2.73 ± 0.01 | 6 ± 2 |
| | 1 | Zr—Si | 3.8 ± 0.1 | 2.84 ± 0.01 | 5 ± 2 |
| | 2 | Zr—Zr | 6.2 ± 0.1 | 3.65 ± 0.01 | 51 ± 4 |

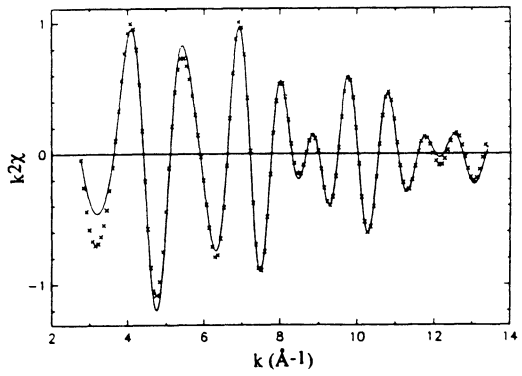


FIG. 5. Comparison of $k^2\chi(k)$ for the experimental data(solid line) and a nonlinear least-squares fit (crosses) for the 650°C annealed Zr/Si film.

the fitting results of films are summarized in Table 1. Error bars are estimated from doubling the variances in nonlinear least-squares fitting. Figure 5 shows the EXAFS structure of the isolated first two shells of the Zr/Si film annealed at 650°C and its fit. The as-deposited Zr film on the Si(111) substrate, although exibiting a reduction in coordination number and larger Debye-Waller factor, is basically Zr metal, if compared with the fitting parameters of Zr foil. The composition of the films annealed above 550°C is mainly $ZrSi_2$. The coordination numbers of the Zr-Si shells of the 550°C and 650°C annealed films are slightly lower than 6.0 and 4.0 respectively, and the Debye-Waller factors are much higher than those of the higher annealing temperature (800°C and 900°C) films. The coordination numbers at 3.7 Å are obviously higher than those of the higher annealing temperature films, and there is an additional Zr-Zr shell at a distance of about 3.3 Å, with the coordination number of 1.4 and 0.2 respectively. The 550°C and 650°C annealed films seem to contain some residual Zr metal or different form of Zr silicide other than Zr disilicide. This is also supported by the XANES structual change between 600°C and 700°C. As the temperature becomes higher than 800°C, the small shell at 3.3 Å disappears, and the Debye-Waller factors of the Zr-Si shells are getting very small. The coordination numbers and distances are very close to those of $ZrSi_2$ crystal structure.

## 4. CONCLUSIONS

The 100 Å Zr film as-deposited on a Si(111) substrate is mainly Zr metal. As the annealing temperature increases, the reaction takes place between the temperature of 350°C and 375°C. Films annealed between 400°C and 650°C consist of a mixture of $ZrSi_2$ C49 structure, residual Zr metal and other Zr silicides. At annealing temperatures higher than 700°C, the films are fully reacted with the silicon substrate and form the $ZrSi_2$ C49 structure. As the temperature increases, the films become more ordered. At the annealing temperatures higher than 850°C, the $ZrSi_2$ film nucleates into islands and the Si substrate starts to appear on the surface. Therefore, the best annealing temperature range to form uniform and large areal coverage $ZrSi_2$ film is between 700°C and 800°C.

## 5. ACKNOWLEDGMENT

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