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Co $L_{3,2}$-edge and multi-detection channel XAFS studies of Co–Si interactions

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We report a high-resolution X-ray absorption fine structure (XAFS) study at the Co $L_{3,2}$-edge for two Co-Si systems: Bulk Co§i and Co/Si(100); the latter was a series of Co-Si films prepared by annealing Co/Si(100) at various stages of a silicidation process. Both total electron yield (TEY) and fluorescence yield (FLY) were used for the measurements. Since TEY and FLY have distinctly different sampling depths at these photon energies, they monitor preferentially the surface/near surface region and the bulk of the specimen respectively. We will also show that these results, together with previous measurements of the same films at the Co *K*-edge, Si *K*- and $L_{3,2}$-edges, provide valuable information about the evolution of the structure and bonding of the Co/Si(100) based Co-Si film formation during the silicidation process.

Keywords: cobalt silicide, thin films, Co L-edge, total electron yield, fluorescence yield

1. Introduction

Metal silicides have found applications in the microelectronics mainly as low resistance contacts to the source, drain and gate. $TiSi_2$ and $CoSi_2$ are the most widely used silicides for these contacts (Murarka, 1983; Maex, 1993). As the tendency to scale device size down continues, questions of the chemical uniformity and electronic properties of small silicide features compared to the bulk have great bearing on device performance.

We have undertaken a study of a series of $CoSi_2$ thin film samples prepared on Si(100) wafers under different conditions using Co $L_{3,2}$-edge X-ray absorption near edge spectroscopy (XANES). The objectives are twofold: 1) to monitor the product of salicidation (self-aligned-silicidation) of a blanket film and 2) to demonstrate the capability of a multi- detection channel technique in XAFS measurements in the soft X-ray region. By measuring the XANES of the films using both total electron yield (TEY) and fluorescence yield (FLY) detection we can probe changes in the composition of the films at various depths.

The total electron yield technique detects primarily Auger and secondary electrons, which have short mean escape depth in solids. For example, the Co *L*-edge Auger has energies of ~700 eV and a corresponding 1/e attenuation length of ~ 2nm while secondary electrons always have longer attenuation lengths (~3 - 5 nm for 0 - 20 eV secondary electrons for example). Thus the extent of the region TEY probes depends largely on the energy of the Auger electrons (Naftel, 1998), the experimental configuration and the condition of the surface. For a Si thin film (e.g 100 nm thick), TEY at Si $L_{3,2}$-edge (~100 eV) is very surface sensitive (~80 eV Auger electrons, an attenuation length of ~0.6 nm) while at the Si K-edge (~1840 eV), TEY is more bulk sensitive (~1740 eV Auger electron, an attenuation depth of ~ 2.5 nm). Glancing incidence of the photon beam would also increase the surface sensitivity. Thus following the procedure of Kasrai (Kasrai, et al. 1996) we estimate that the sampling depth in TEY at the Co $L_{3,2}$-edge will be of ~10 nm. Fluorescence yield has a larger sampling depth as the attenuation of the fluorescent X-rays is only slightly less than the attenuation of the incident photons (Kasrai et al. 1996). The one-absorption length above the Co L_3-edge for Co metal is ~ 100 nm (Henke et al. 1982) which is comparable to the thickness of the films under investigation, therefore FLY is sensitive to the bulk of the film (Böske et al. 1994).

This study at the Co $L_{3,2}$-edge is an extension of our previous studies of $CoSi_2$ and $NiSi_2$ films using the Metal K-edge, Si $L_{3,2}$- and Si K-edges (Naftel *et al*, 1998a and b). In those studies, we demonstrated that XANES measurements at a number of core-levels using multiple detection schemes facilitates the nondestructive characterization of the chemical uniformity of the film and buried interfaces.

2. Experiment

The $CoSi_2$ ingot was prepared by the materials preparation group at McMaster University based on the phase diagram. The thin film samples were prepared at Northern Telecom using a DC sputtering technique. 55.6 nm of Co were deposited onto clean Si(100) wafers. The as-deposited sample was then annealed in a two step process in nitrogen atmosphere (Saran & Naem, 1995). Table I lists the preparation conditions of the samples. No attempt was made to remove the native oxide from the thin film samples. The bulk ingot was mechanically scrapped with a diamond file before introduction to the experimental chamber to remove the native oxide.

The spectra were taken at the Synchrotron Radiation Center (SRC), the University of Wisconsin-Madison using the High Energy Resolution Monochromator (HERMON) at a resolution of ~ 3000. Total electron yield measurements were made using sample current while the fluorescence yield measurements were carried out with a channel plate detector (Kasrai, 1996, Naftel, 1998b).

Table 1.
Sample preparation conditions

Sample	Description
$CoSi_2$	Bulk Ingot (arc-melt followed by annealing)
Co-Si (1)	Co film, as-deposited at room temperature
Co-Si (2)	Co film, annealed 450°C/60 sec. then 690°C/60 sec.
Co-Si (3)	Co film, annealed 550°C/60 sec. then 690°C/60 sec.

3. Results and discussion

Figure 1 shows the FLY Co $L_{3,2}$-edge spectra for the $CoSi_2$ ingot and the films. All spectra have had a linear pre-edge background removed. Since the sampling depth of the fluorescence technique is larger than the thickness of the film, FLY is dominated by the bulk characteristics of the films.

The L_3-edge portion of the spectra of the bulk sample has a three peak structure which corresponds to those reported elsewhere (Pong *et al.* 1996; Lerch *et al.* 1992) and our recent calculation (Naftel et al. 1999). The spectra of both annealed films (Co-Si (2) and (3)) are similar to that of the bulk sample indicating that the bulk of silicide produced in the films is predominately $CoSi_2$. The spectra of the as-deposited film, however, shows only one main peak with an asymmetric tail at higher photon energies, this corresponds to the expected spectra of Co metal (Böske *et al.* 1994, Naftel et al. 1999).

Figure 2 shows the TEY Co $L_{3,2}$-edge spectra of the $CoSi_2$ ingot and the three films. The spectra have been scaled to the maximum of the peak heights after pre-edge background removal. The TEY of the CoSi$_2$ ingot is similar to that recorded in FLY in spectral pattern but shows more pronounced features. This is due to the fact that the FLY spectrum was distorted due to self-absorption. The effect of self-absorption is less severe for thin films as borne out in the as-deposited sample. It is interesting to note that the TEY spectra for the silicide films Co-Si (2) and Co-Si (3) are noisier than their FLY counter parts despite the fact that TEY usually has much better counting statistics. This anomaly is due to the fact that the surface of the film is covered with silicon oxide which has a dominant presence over the metal oxide as reported previously (Naftel et al. 1998a, 1998b). Since TEY is surface sensitive, the presence of surface silicon oxide only contribute to a large background at the Co *L*-edge. The TEY for the as-deposited film exhibits a spectrum similar to that reported before (Pong *et al.* 1996) for Co metal except for a slightly better resolution in the present study.

Close examination reveals that the TEY spectra of the films (Fig.2) still have the multiple peak structure similar to those of FLY but the intensity of the lowest photon energy peak varies significantly. This is most evident in the film initially annealed at 450 °C in which the first peak is the most intense in contrast to its FLY spectrum where the first peak is the least intense (Fig.1). Because the FLY spectra indicate that the films are predominantly CoSi$_2$ in the bulk, the TEY spectra must indicate the presence of phases other than CoSi$_2$ in the surface and near surface region of the film. Semi-quantitatively, it is reasonable to assume that TEY for the films is a superposition of the bulk and the surface/near surface phase. Therefore, to a good approximation, we can obtain the surface spectrum of the silicide films by taking the film spectrum (TEY), scale it to the background between the L_3- and L_2-edges (edge jump), then subtracte from it the normalized TEY spectrum of the bulk CoSi$_2$ (ingot). The results are shown in Figure 3.

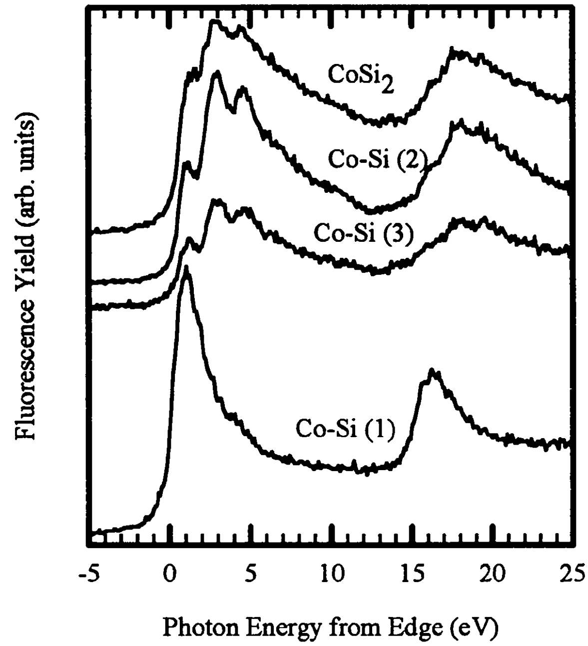

Figure 1.
Co L$_{3,2}$-edge spectra taken in FLY mode. Spectra have been shifted vertically for clarity.

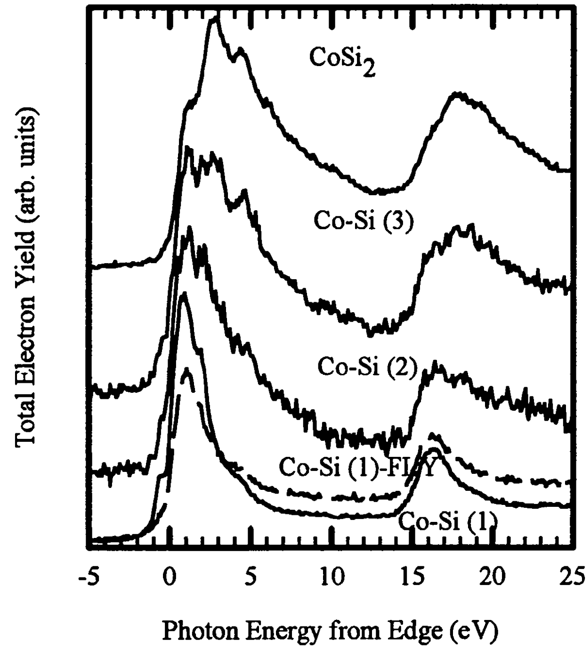

Figure 2.
Co L$_{3,2}$-edge spectra taken in TEY mode and the FLY spectrum of the as-deposited film. Spectra have been shifted vertically for clarity.

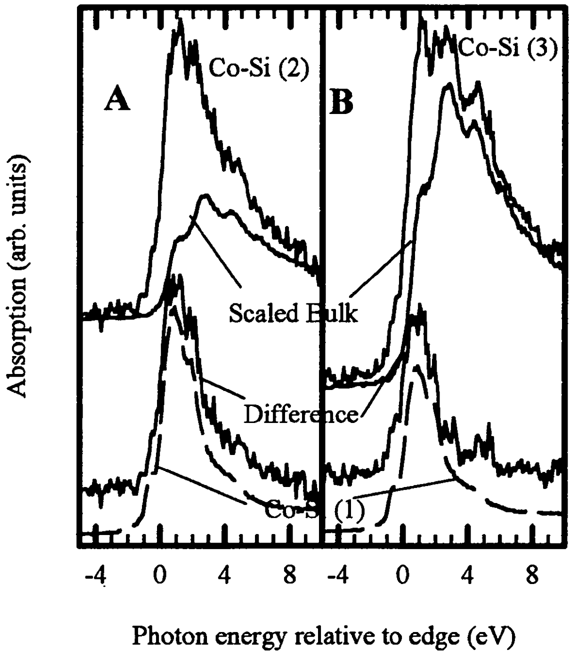

Figure 3.
Subtraction of scaled bulk CoSi$_2$ spectra from the TEY spectra of the annealed Co-Si films compared to the spectra of the as-deposited film. A) Co-Si (2) and B) Co-Si (3).

The difference spectra clearly match the spectrum of the as-deposited Co film. Thus, the second phase seen in the annealed films is primarily Co metal at the surface (Pong et al. 1996).

4. Conclusions

We have studied a series of $CoSi_2$ films, prepared under different annealing conditions, on Si(100) wafers as well as a $CoSi_2$ ingot. We found that the Co layer deposited on the Si remained unreacted with silicon at room temperature. Upon annealing the Co layer reacts to form $CoSi_2$ predominantly, although the presence of some Co or Co rich silicide at the surface of the sample is detected.

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