XAFS Studies of TiSi_2 and CoSi_2 Thin Films at the Ti, Co and Si K-Edge

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Abstract: XAFS measurements at the metal and Si K-edge have been made for a series of TiSi_2 and CoSi_2 blanket silicide films as well as bulk CoSi_2 and TiSi_2 . It was found that the films have essentially the same structure as the bulk TiSi_2 and CoSi_2 , and that the Si XANES exhibit very rich structures. Both the materials characterization and spectroscopy aspects of the XAFS are discussed.

1. INTRODUCTION

TiSi_2 , as well as other silicides, has found applications in microelectronic devices as low resistance contacts, Schottky barrier clamps and interconnects [1]. As the device technology approaches submicron size, research in new materials and processes involving smaller dimensions becomes more important. One of the fundamental questions concerning the performance of the materials, when its dimension is scaled down, is the chemical uniformity, structure and electronic properties compared to that of the bulk.

In this paper, we report a XAFS study of bulk TiSi_2 , CoSi_2 and their blanket silicide (self-aligned silicide) films prepared under different conditions. Of particular interest is the Si K-edge results using a total electron yield technique in which the combined X-ray and electron attenuation length allows for the detection of both the surface and the bulk of the film. The Si K-edge XANES is compared with a densities of states calculation for CoSi_2 . The metal K-edge XAFS results are also discussed.

2. EXPERIMENTAL

TiSi_2 and CoSi_2 ingots were prepared by the Materials Preparation Group at McMaster University using standard procedures. The CoSi_2 and TiSi_2 silicide films were prepared at Northern Telecom using a DC sputtering technique. Co (55.6nm) and Ti (50nm) were deposited on clean Si(100) wafers followed by a two step thermal annealing in a nitrogen ambient as described previously [2,3]. The first step is a low temperature anneal (60 sec) at 450°C or 550°C for CoSi_2 and 625°C or 700°C for TiSi_2 . The second step anneal (also 60 sec) is at 790°C for TiSi_2 and 690°C for CoSi_2 .

The Si K-edge XAFS measurements were made in a Total Electron Yield (TEY) mode at the soft X-ray Double Crystal Monochromator beamline of the Canadian Synchrotron Radiation Facility at the Synchrotron Radiation Center-University of Wisconsin, Madison. InSb(111) was used as monochromator crystals. Co and Ti K-edge measurements were made using a He-TEY detector at the X11A beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. In the Si K-edge measurements, silicide specimens were degreased before introduction into the vacuum chamber and in the case of the bulk specimens, spectra were recorded for both the ambient and the clean (scraped with a diamond file) sample.

3. RESULTS AND DISCUSSION

Fig. 1a shows the Si K-edge XANES of a CoSi_2 film (550°C-690°C anneal) and an ambient bulk CoSi_2 , the XANES for a Si(100) wafer and a SiO_2 standard are also shown (the spectrometer is calibrated by setting the Si(100) threshold energy at 1839.1 eV). The most noticeable feature is the sharp spike at ~1847 eV which is characteristic of silicon oxide as seen in the SiO_2 spectrum. It is possible to remove the surface oxide contribution by subtracting a properly scaled SiO_2 spectrum. Results of such a procedure are shown in Fig. 1b. It can be seen that the XANES for the ambient CoSi_2 , with SiO_2 removed resembles closely to that of the clean CoSi_2 sample. The XANES for the CoSi_2 film with SiO_2 contribution removed is also similar to that of the clean bulk CoSi_2 sample.

It should be noted that at these film thickness (several 10^2 nm), the Si(100) substrate will contribute little since the TEY technique has a probing depth of ~70 nm at the Si K-edge [4]. Thus all the signal in our measurement comes from the silicide film. Based on ref. 4, a silicon oxide thickness of ~7 nm is estimated. It is interesting to note that the film with a lower first anneal temperature (450°C) exhibits a more intense oxide peak (by 40% relative to the edge jump) than the high temperature specimen shown above.

Fig. 2a and 2b show the corresponding spectra for the TiSi_2 series. Except for the less intense oxide peak, the XANES look strikingly similar to that for CoSi_2 , indicating similar local symmetry for Si in both silicides. The reduction in oxide signal shows that Si in TiSi_2 is less susceptible to oxidation than in CoSi_2 . A thickness of ~5 nm for the silicon oxide on the TiSi_2 film was estimated. As in the case of the CoSi_2 system, the film with a lower first anneal temperature (625°C) has a thicker oxide layer.

Fig.1: Si K-edge XANES for (a) ambient CoSi_2 ; (b) scraped CoSi_2 (bulk) and film (-oxide contribution), (see text).

Fig.2: Si K-edge XANES for (a) ambient TiSi_2 ; (b) scraped TiSi_2 (bulk) and film (-oxide contribution), (see text).

Fig.3: Si K-edge XANES and first derivatives; thresholds are indicated with bars, arrows show the resonances; insert shows the Si p-DOS from ref.5

Fig.4: XAFS of (a) 200Å $\text{Co}/\text{Si}(100)$, (b) CoSi_2 (bulk) (c) CoSi_2 film (550-690°C), (d) CoSi_2 film (450-690°C)

Shown in Fig.3 is the expanded region near the threshold for both bulk silicides. The calculated partial densities of states (DOS) of Si p character (insert) for CoSi_2 [5] is also shown. Two features are noted: first the threshold energy exhibits a chemical shift: TiSi_2 (-1 eV) < CoSi_2 (-6 eV) < $\text{Si}(100)$ as expected based on the electronegativity difference; second there are clearly three well-defined resonances above the threshold (within ~ 4 eV) in good agreement with the calculated Si p-DOS [5,6].

Finally, we report the Ti and Co K-edge results which show that all the films exhibit identical EXAFS as those of the bulk silicides. The surface contribution is not noticeable since the technique is more bulk sensitive in the hard X-ray region. A series of Co K-edge spectra for a typical run is shown in Fig.4

4. SUMMARY AND CONCLUSION

We have reported some observations of a Si and metal K-edge XAFS study for a series of blanket TiSi_2 and CoSi_2 silicide films and the corresponding bulk samples. All the films appear to have the same structure as that of the bulk. The film surfaces are covered with several nm of SiO_2 , not insignificant comparing to the total thickness of the film. The Si K-edge XANES exhibits remarkable rich structures which are attributed to densities of states effects.

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