XAFS studies of the formation of cobalt silicide on $\left(\sqrt{3}\times\sqrt{3}\right)$ SiC(0001)

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Thin Co films (1-8 nm) were directly, sequentially, and co-deposited with Si (3.6-29.2 nm) on the $\left(\sqrt{3}\times\sqrt{3}\right)$-R30° reconstruction of 6H-SiC(0001). The films were annealed over a temperature range of 823-1373K and investigated with XAFS, XPS, AES and AFM. After annealing up to 1373K directly deposited Co films do not transform entirely to cobalt disilicide and C segregation is observed on the surface of the films. On the other hand, sequentially and co-deposited films do form cobalt disilicide after annealing at 823K, but also show islanding after annealing at 923K.

Keywords: cobalt silicide, silicon carbide, metal-semiconductor contacts, molecular beam epitaxy

1. Introduction

As the need for electronic devices in all areas grows, there is also a growing need for devices in areas of extreme environmental conditions. Because of its unique properties, including high thermal conductivity, SiC presents itself readily for use as a semiconductor in such devices. SiC would prove a useful semiconductor in high-power devices as well as in devices that much operate under conditions of high temperature or high radiation. Research into making SiC a viable semiconductor in such areas has obvious positive ramifications.

The Co/SiC system has been studied by several investigators for the application of both structural composites and contacts for devices (see e.g. Porter *et al.* (1995) and Lundberg & Östling (1996)). Most of these studies focused on directly deposited Co films on SiC and relatively little attention has been paid to sequentially or co-deposited Co/Si films as well as to the different surface reconstructions of the SiC substrate, although it is known that the properties of ohmic contacts and Schottky barrier diodes can strongly depend on the surface characteristics.

In this study, x-ray absorption fine structure (XAFS) and atomic force microscoppy (AFM) have been employed to investigate the surface and interface chemistry as well as the morphology of cobalt silicide films on $\left(\sqrt{3}\times\sqrt{3}\right)$ 6H-SiC(0001).

2. Experiment

The Co films and Co/Si bilayers were deposited on 6H-SiC(0001) wafers (Si face). The wafers were n type and purchased from CREE Research Inc. Tungsten of several microns thickness was sputtered on the back side of each wafer to facilitate *in situ* heating by absorption of infrared radiation. The wafers were exposed to UV/ozone irradiation and then chemically etched with a HF:H_2O:ethanol (1:1:10) solution. The wafers were then loaded into a UHV system, that has a base pressure in the 10^{-10} Torr range. The $\left(\sqrt{3}\times\sqrt{3}\right)$-R30° surface reconstruction as determined by low-energy electron diffraction (LEED) was prepared by *in situ* thermal desorption at 1473K under Si flux of 0.003 nm/sec. Co and Si were deposited in UHV at room temperature followed by thermal annealing for 20 min at 823-1373K. A Si:Co ratio of 3.64 was used for the sequentially and co-deposited films which is the stoichiometric ratio for $CoSi_2$.

The films were studied *in situ* with LEED, Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS). *Ex situ* AFM data were acquired in contact mode with a Park Scientific Autoprobe M5 instrument (typical radius of curvature of the AFM silicon nitride tips are about 10nm).

Ex situ XAFS data of the annealed films were collected at room temperature at the Co K-edge (7709 eV) in the fluorescence mode with a Canberra 13-element Ge detector at beamline X-11A at the National Synchrotron Light Source (NSLS). The incident photon beam was perpendicular to the film sample surface and monochromatized with a double-crystal Si(100) monochromator detuned 30% to suppress higher harmonics. Energy calibration was set to 7709 eV at the Co foil K-edge inflection point. XAFS data analysis was performed with the MacXAFS 4.1 package (Bouldin *et al.*, 1995). Fourier transforms of k^2-weighted XAFS data were done over the wavevector range $k = 3.5\text{-}10.3$ Å^{-1} after pre-edge subtraction, normalisation, background removal, and conversion from energy scale to wave vector, k.

3. Results and Discussion

The Fourier transforms of the k^2-weighted XAFS data for directly deposited films are shown Fig. 1. The spectra for a 8 nm and 2 nm Co film on $\left(\sqrt{3}\times\sqrt{3}\right)$ SiC annealed at 973K as well as standard spectra for Co metal and $CoSi_2$ indicate mainly Co-Co bonds for the direct deposited Co films. The difference in the hight between the metal reference sample and the 8 nm as well as 2 nm film is due to the fact that a small amount of cobalt silicide is forming during annealing. In addition, these films are not epitaxial indicated by a completely diffuse LEED pattern. From a fit of the x-ray absorption near edge structure (XANES) depicted in Fig. 2 it was estimated that the films consist of 70% Co metal and 30% $CoSi_2$, which is consistent with the Fourier transformes shown in Fig. 1.

These results are in agreement with XPS measurements, which show that the Co 2p peaks are not shifting to higher binding energies even after annealing at 1273K. These XPS data and the AES measurements revealed a significant increase of the C peak suggesting that graphitic carbon is forming at the surface of the films. This is in agreement with the literature, which also reports the formation of carbon or graphite on the Co film surface deposited on SiC (Lunderg *et al.* (1993), Porter et al. (1995), Lundberg & Östling (1993)).

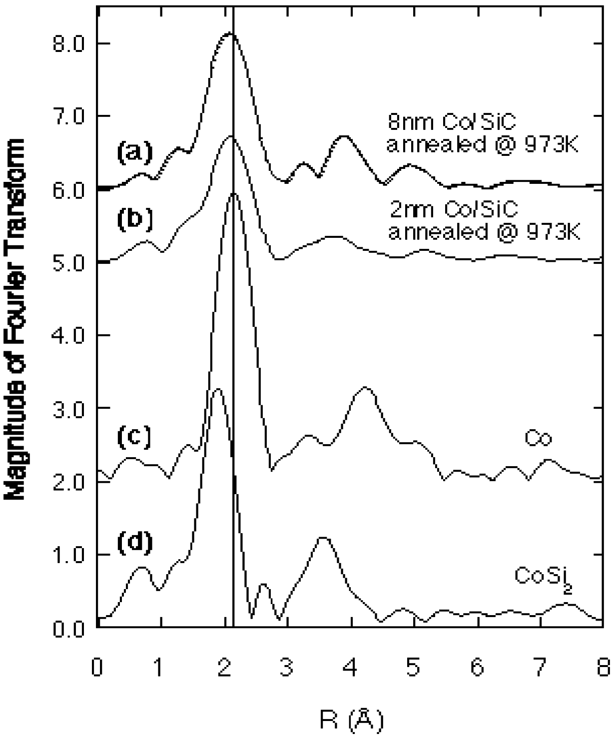

Figure 1
Fourier transform of k^2-weighted XAFS data for (a) 8 nm Co and (b) 2 nm Co on $\left(\sqrt{3}\times\sqrt{3}\right)$ SiC after annealing at 973K, (c) foil and (d) $CoSi_2$.

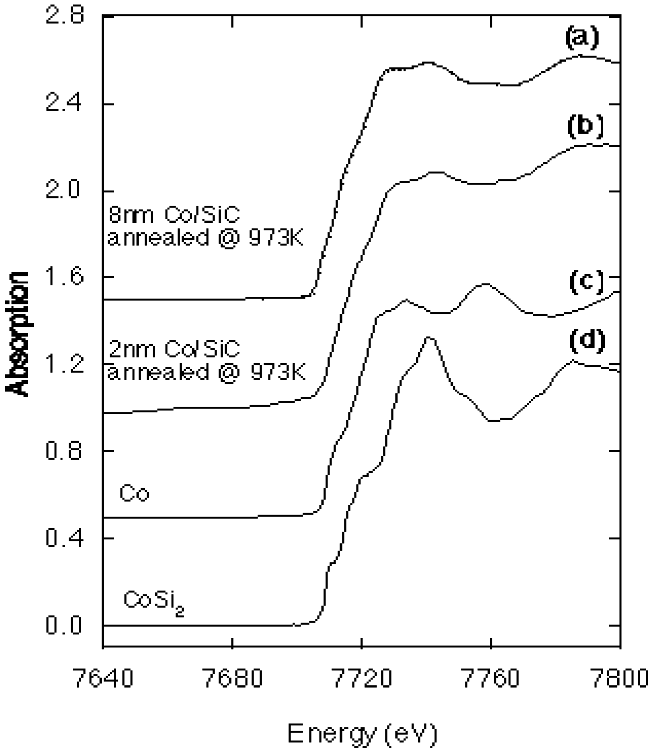

Figure 2
Normalized XANES data for (a) 8 nm Co and (b) 2 nm Co on $\left(\sqrt{3}\times\sqrt{3}\right)$ SiC after annealing at 973K (c) foil and (d) $CoSi_2$.

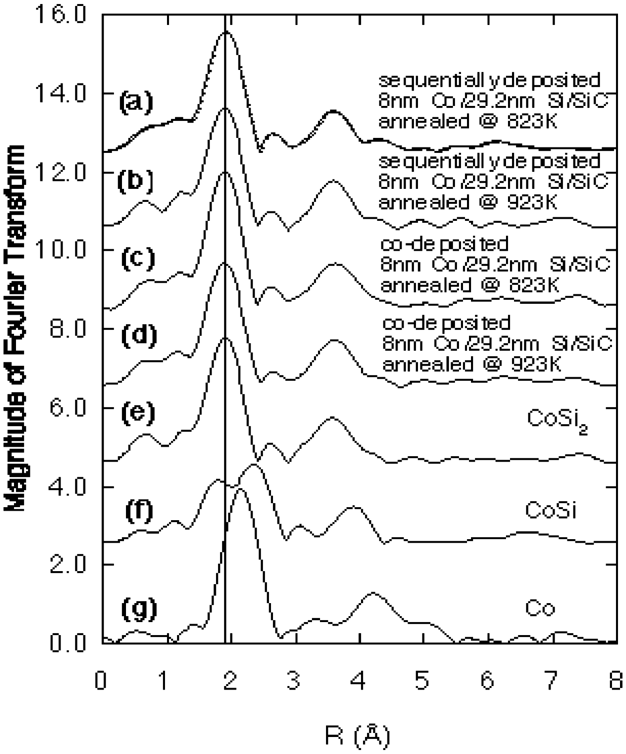

Figure 3
Fourier transform of k^2-weighted XAFS data for 8 nm Co/29.2 nm Si sequentially deposited on $\left(\sqrt{3}\times\sqrt{3}\right)$ SiC after annealing at (a) 823K, (b) 923K, 8 nm Co/29.2 nm Si sequentially deposited on $\left(\sqrt{3}\times\sqrt{3}\right)$ SiC after annealing at (c) 823K, (d) 923K, (e) $CoSi_2$, (f) CoSi and (g) Co foil.

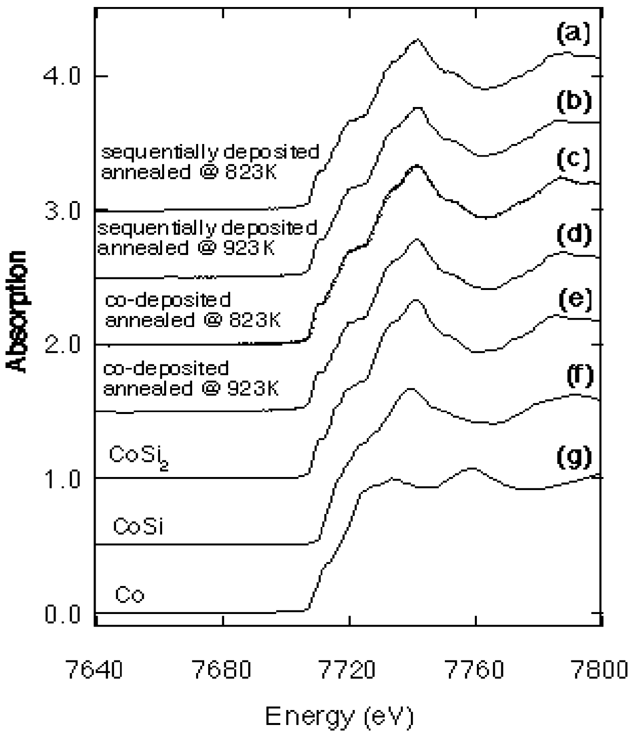

Figure 4
Normalized XANES data for 8 nm Co/29.2 nm Si sequentially deposited on $\left(\sqrt{3}\times\sqrt{3}\right)$ SiC after annealing at (a) 823K, (b) 923K, 8 nm Co/29.2 nm Si sequentially deposited on $\left(\sqrt{3}\times\sqrt{3}\right)$ SiC after annealing at (c) 823K, (d) 923K, (e) $CoSi_2$, (f) CoSi and (g) Co foil.

Several films were grown sequentially and by co-deposition of Si and Co with a thickness ratio of 3.64:1 onto $\left(\sqrt{3}\times\sqrt{3}\right)$ 6H-SiC(0001). These films form $CoSi_2$ during annealing at 823K or 923K as is unambiguously shown by the XAFS and XANES data depicted in Fig. 3 and Fig. 4, respectively. The fact that the bilayers and co-deposited films show the same features in the Fourier transform and XANES as the $CoSi_2$ reference sample rules out the possibility that the films contain significant amounts of CoSi or Co metal (> 5%). Since XAFS and XANES data were collected *ex situ*, some monolayers of the films might be oxydized. However, the similarity between the XANES data of the films and the $CoSi_2$ reference sample indicates that the oxygen contamination is negligible.

Long range order is indicated by the appearance of higher shells. However, the LEED pattern appeared diffuse indicating that these films consist of grains smaller than the correlation length for LEED, which is10 nm.

Shown in Fig. 5 are *ex situ* AFM images taken from sequentially deposited 8 nm Co and 29.2 nm Si on $\left(\sqrt{3}\times\sqrt{3}\right)$ SiC annealed at 823K and 923K. The bilayer annealed at 823K forms a smooth $CoSi_2$ film with a RMS roughness of 2.2 nm. In contrast, for the film annealed at 923K islands were observed with large substrate regions not covered. The appearance of a $\left(\sqrt{3}\times\sqrt{3}\right)$-R30° LEED pattern indicates that the $\left(\sqrt{3}\times\sqrt{3}\right)$ SiC surface reconstruction remains unaffected by the formation of $CoSi_2$.

4. Conclusion

A structural and morphological study of directly, sequentially and co-deposited cobalt silicide films on $\left(\sqrt{3}\times\sqrt{3}\right)$-R30° SiC(0001) has been performed. Directly deposited films on $\left(\sqrt{3}\times\sqrt{3}\right)$ SiC do not form $CoSi_2$. After annealing up to 1273K these films contain mainly Co metal as well as graphitic carbon which was detected at the film surface. Sequentially and co-deposited films form smooth polycrystalline $CoSi_2$ film during annealing 823K with a RMS roughness of 2.2 nm. No C segregation occurs. Further annealing at 923K results in islanding of the $CoSi_2$ film exposing large areas of the underlying $\left(\sqrt{3}\times\sqrt{3}\right)$ SiC substrate.

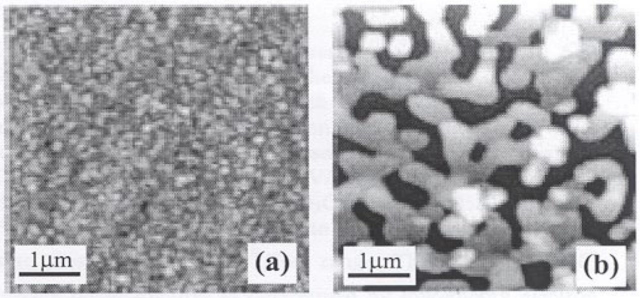

Figure 5
AFM scans of sequentially deposited 8 nm Co/29.2 nm Si on $\left(\sqrt{3}\times\sqrt{3}\right)$ SiC annealing at (a) 823K, (b) 923K. The scan size in both cases is $5\times5\,\mu m$. The black-to-white scales are 17.8 and 119 nm, respectively.

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