# Growth of epitaxial $CoSi_2$ on $6H\text{-}SiC(0001)_{Si}$

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# Growth of epitaxial $CoSi_2$ on 6H-SiC$(0001)_{Si}$

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Epitaxial growth of (111)-oriented $CoSi_2$ has been achieved on a scratch-free 6H-SiC$(0001)_{Si}$ substrate. The surface was prepared using atmospheric hydrogen etching and ultrahigh vacuum Si cleaning. A high-quality $CoSi_2$ thin film was obtained by a modified template method and co-deposition of Co and Si at 550 °C. The structure and morphology of the film is studied by means of reflection high electron energy diffraction, x-ray absorption fine structure, x-ray diffraction, and atomic force microscopy. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1412842]

## I. INTRODUCTION

The high thermal stability and low resistivity of cobalt disilicide ($CoSi_2$) makes it an attractive contact material to silicon carbide (SiC), which is currently of great interest for high temperature and high power semiconductor device fabrication.[1] Epitaxial contacts to SiC may exhibit more uniform electronic properties, be stable at higher temperatures and enable more complex epitaxial microstructures.

Since $CoSi_2$ and 6H-SiC have different crystal structures (cubic and hexagonal) it has been a substantial challenge to achieve epitaxial growth. However, cubic $CoSi_2$ does exhibit three-fold symmetry along the (111) axis which matches the symmetry of the SiC planes. We considered the lattice matching of the $CoSi_2$ (111) plane and (0001) plane of the SiC. The in-plane lattice vector of the $CoSi_2$ (111) plane, when rotated by 30°, can be projected onto the doubled SiC in-plane lattice vector with a mismatch of ~6%. Thus epitaxy may be anticipated.

Detailed studies of the structural and electrical properties of directly deposited Co films on SiC have been performed.[2–9] It has been shown that Si/Co/SiC[3] or Co/Si/SiC[7] bilayers are needed to form $CoSi_2$ films on SiC without consuming Si from the SiC substrate, which causes graphite segregation. In a previous study of sequentially and co-deposited Co and Si films on Si etched 6H-SiC(0001) it was demonstrated that annealing at 550 °C resulted in the formation of polycrystalline $CoSi_2$ thin films whereas annealing at 650 °C results in islanding.[7,8] In addition, the use of template layers prior to co-deposition of Co and Si at 550 °C resulted in $CoSi_2$ films along with $CoSi_2$ clusters agglomerated at the polishing scratches of the SiC substrate and large, virtually featureless areas. It was postulated that by removing the SiC substrate polishing scratches it might be possible to suppress the agglomeration and achieve smooth epitaxial $CoSi_2$ films.

The present work demonstrated a method to attain epitaxial $CoSi_2$ metal contacts to 6H-SiC$(0001)_{Si}$. The 6H-SiC$(0001)_{Si}$ surface was prepared with a two-step method similar to the procedure used by Xue *et al.*[10] First, typical polishing scratches of the 6H-SiC$(0001)_{Si}$ substrate were removed by atmospheric $H_2$ etching resulting in a stepped surface morphology. In a second step, oxides and other contaminants were eliminated by *in situ* ultrahigh vacuum (UHV) Si molecular beam etching. Finally, epitaxial growth of (111)-oriented $CoSi_2$ thin films on the SiC surface was achieved by a template method and co-deposition of Co and Si at 550 °C.

## II. EXPERIMENT

The majority of the experiments were carried out at the National Synchrotron Light Source (NSLS). The SiC substrate and the $CoSi_2$ films were prepared in a UHV integrated surface analysis and growth system, that has a base pressure in the low $10^{-10}$ Torr range allowing *in situ* transfer between facilities for molecular beam epitaxy (MBE), reflection high-energy electron diffraction (RHEED), Auger electron spectroscopy (AES), and x-ray absorption fine structure (XAFS).

On axis, *n*-type 6H-SiC$(0001)_{Si}$ wafers were obtained from CREE Research Inc. Following an *ex situ* Hartree–Fock (HF) clean the wafers were treated with atmospheric $H_2$ while field at 1600 °C for 20 min. After UV/ozone irradiation exposure and chemical etching with an HF:$H_2O$:ethanol (1:1:10) solution, the wafers were further prepared in a UHV system by *in situ* thermal desorption at 1200 °C for 15 min under a Si flux of 0.003 nm/s (i.e., Si molecular beam etching).

A template method was used to control the nucleation of $CoSi_2$ at the film–substrate interface and, therefore, the subsequent film morphology. A template approach was also used by Boyanov *et al.*[11] to prepare smooth $CoSi_2$ films on strained epitaxial layers of $Si_{1-x}Ge_x(001)$. In order to prevent interaction of the template with the substrate a thin sacrifical Si layer was used between the initial Co layer and the substrate. Accordingly, the template structure consisted of 2

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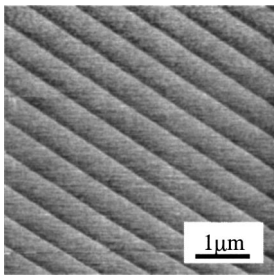


FIG. 1. AFM scan of hydrogen etched 6H-SiC$(0001)_{Si}$ surface. The scan size is $5\times5$ $\mu m^2$ and the black-to-white scale is 2.5 nm.

FIG. 2. RHEED pattern for the 6H-SiC$(0001)_{Si}$ surface prepared by $H_2$ and UHV Si etching. The electron beam was incident along the SiC[1120] azimuth.

ML Si/1 ML Co/2 ML Si deposited at room temperature. The template was capped with a thin co-deposited film of 0.2 nm Co and 0.73 nm Si prior to further film deposition. The slight excess of Si in the initial layer should inhibit direct reaction of the Co with the SiC substrate.

After preparing the template structure, a stoichiometric $CoSi_2$ layer was deposited at 550 °C, the layer included 8 nm of Co and 29.2 nm of Si (Si:Co thickness ratio of 3.64 to obtain $CoSi_2$). The thicknesses were measured with a quartz crystal monitor during deposition. Deposition rates of the system have been calibrated with profilometry, atomic force microscopy (AFM), transmission electron microscopy (TEM), and Rutherford backscattering spectroscopy (RBS). We estimate the relative concentration accuracy for the thin films to be about 10%. Oxygen surface contamination was below the AES detection limits at all stages after the UHV surface preparation.

The $CoSi_2$ films were characterized *ex situ* with x-ray absorption fine structure (XAFS), x-ray diffraction (XRD), and atomic force microscopy (AFM). The Co K-edge XAFS data was collected at room temperature in the fluorescence mode with a Canberra 13-element Ge detector at beamline X-11A at the National Synchrotron Light Source (NSLS). 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.[12] Fourier transforms of $k^2$-weighted XAFS data were performed over the wave vector range $k = 3.5–10.3$ $Å^{-1}$ after pre-edge subtraction, normalization, background removal, and conversion from energy scale to wave vector, $k$.

XRD data were collected with a Bruker D500 4-circle diffractometer equipped with an area detector. AFM data were acquired in contact mode with a Park Scientific Autoprobe M5 instrument.

## III. RESULTS AND DISCUSSION

Shown in Fig. 1 is an AFM image collected from the 6H-SiC$(0001)_{Si}$ surface after $H_2$ and Si etching. A uniform distribution of terraces about 830 nm in width and separated by straight steps decorates the SiC surface. All steps are measured to be 1.5 nm in height corresponding to the vertical lattice parameter of the 6H-SiC$(0001)_{Si}$ substrate. Assuming that the terrace width is due to a slight miscut of the SiC substrate one obtains a miscut angle of 0.1°. Xue *et al.*[10] have speculated that the equidistant step morphology could be the result of repulsive interaction between the steps.[13] Since the same terrace widths and step heights were also observed just after atmospheric $H_2$ etching, one may conclude that the UHV Si molecular beam etching does not affect the step arrangement. However, the process removes contaminants and results in atomically flat terraces.[9]

A RHEED pattern of this surface is shown in Fig. 2. The diffraction spots appear very sharp, indicating a well ordered surface lattice. The pattern displays a $(3\times3)$ surface reconstruction. The 6H-SiC$(0001)_{Si}$ surface prepared under the same conditions, but without $H_2$ etching formed a $(\sqrt{3}\times\sqrt{3})$ surface reconstruction.[7]

The local structure of the film was investigated with XAFS. The Fourier transform of the XAFS data from the film as well as standard spectra for $CoSi_2$, CoSi, and Co metal are shown in Fig. 3. The Co, CoSi, and $CoSi_2$ standards were obtained from deposition of thick Co films (100 nm) on Si substrates. The depositions were at room temperature, and films were annealed at ~450 °C and ~650 °C to form CoSi and $CoSi_2$, respectively. The crystal structures were verified with XRD, which displayed a polycrystalline pattern indicating no preferred orientation. The XAFS spectrum of the film on SiC displays the same features as the $CoSi_2$ reference sample indicating that the film consists mostly of $CoSi_2$. Long-range order as indicated by the appearance of higher shells is consistent with well ordered

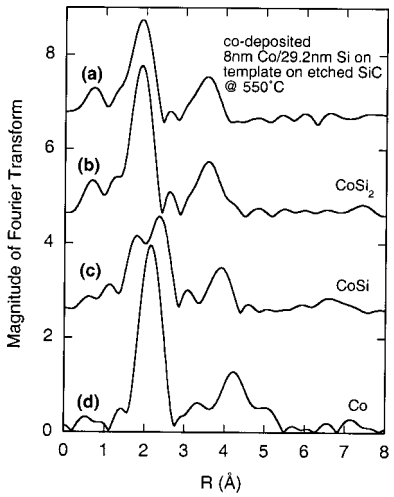


FIG. 3. Fourier transform of $k^2$-weighted XAFS data for (a) 8 nm Co/29.2 nm Si co-deposited on a layered template/6H-SiC$(0001)_{Si}$ at 550 °C, (b) $CoSi_2$, (c) CoSi, and (d) Co foil.

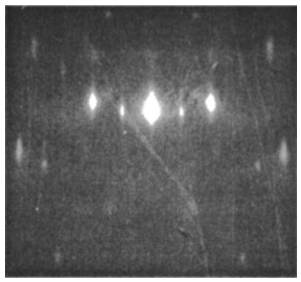

FIG. 4. RHEED pattern of 8 nm Co/29.2 nm Si co-deposited on a layered template/6H-SiC(0001)$_{Si}$ at 550 °C. The electron beam was incident along the SiC[1120] azimuth.

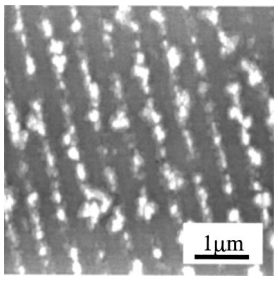


FIG. 6. AFM scan of 8 nm Co/29.2 nm Si co-deposited on a layered template/6H-SiC(0001)$_{Si}$ at 550 °C. The scan size is 5×5 $\mu m^2$ and the black-to-white scale is 58 nm.

crystalline domains. We note that XAFS is sensitive to the local order and will not be significantly affected by epitaxial orientation. To gain a quantitative estimate of the fraction of $CoSi_2$ represented by the results, the x-ray absorption near edge structure (XANES) was fit using an approach described previously,[8] and the experimental results were accurately represented by the XANES of the $CoSi_2$ standard. Within the uncertainty of the fitting process this suggests that less than 10% of the film is in a structure different from $CoSi_2$.

The AES spectra of the film showed only cobalt and silicon peaks, i.e., the film was free of contaminants and did not form islands or pinholes as would be indicated by the appearance of a carbon substrate peak.

The RHEED diffraction of the 8 nm Co/29.2 nm Si film (Fig. 4) displays a (2×2) surface periodicity. However, some bulklike diffraction spots were observed which were attributed to scattering from asperities on the film surface. While other effects can occur in RHEED, the results are certainly consistent with epitaxial $CoSi_2$ layers on the SiC terraces.

The orientation of the film was determined with XRD. An intense $CoSi_2$(111) peak was clearly visible (Fig. 5) indicating that the $CoSi_2$ is (111) oriented or textured. No other $CoSi_2$ peaks were detected in the $15° \leqslant 2\theta \leqslant 70°$ range.

Finally, the surface morphology of the $CoSi_2$ film was investigated with AFM (Fig. 6). Clusters forming chains along the step edges separate the long striped terraces. The clusters extend ~50 nm above the terrace surface, which is much higher than the 1.5 nm step height of the clean surface.

Our prior study of $CoSi_2$ formation on surfaces with polish scratches[7] indicated that the clusters accounted for approximately one fourth of the deposited $CoSi_2$ volume, and analysis of the image in Fig. 6 suggests that the agglomerated islands are about one fifth of the deposited film. The step edges apparently contribute to an instability that leads to the formation of the agglomerated cluster chains. Whether strain or surface energy or other kinetic effects cause this agglomeration is still undetermined.

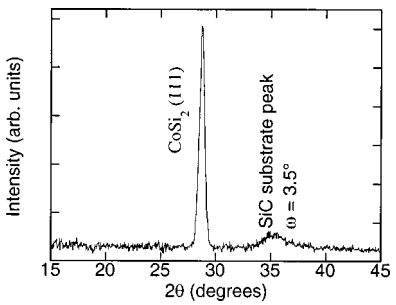


FIG. 5. XRD scan of 8 nm Co/29.2 nm Si co-deposited on a layered template/6H-SiC(0001)$_{Si}$ at 550 °C. The SiC substrate peak was suppressed by tilting the substrate 3.5° away from the normal (i.e., $\omega = 3.5°$).

The XAFS, AES, RHEED, and XRD results taken together indicate that the terraces are covered with an epitaxial layer of $CoSi_2$ and that the clusters are also apparently epitaxial or textured. The AES indicates that the surfaces are completely covered with a Co–Si film. The XAFS indicates that the film is predominantly $CoSi_2$. The AFM shows smooth, apparently single domain layers on each terrace with agglomerated islands at the step edges. The XRD shows (111) orientation with no signature of other phases suggesting that both the islands and terraces are similarly oriented or textured.

We note that the epitaxial layers were deposited at 550 °C without any post deposition annealing. Our prior study showed that films deposited or annealed at 650 °C on polished substrates showed islanding which suggests that these films will also degrade at this temperature.[7] Further research is necessary to explore the thermal stability of the layers.

Most integrated circuit technologies are not designed to operate at temperatures above 250 °C, but high-temperature devices capable of operating at temperatures ranging from 350 to 550 °C are highly desirable,[1] and the low-resistivity $CoSi_2$ metal contact[14] to 6H-SiC(0001)$_{Si}$ achieved in this study seems to be suited for this environment. In addition, the arrangement of the cluster chains, which is controllable through the substrate miscut, may even be useful for future nanostructure devices.

## IV. CONCLUSIONS

In summary, we have studied the growth of $CoSi_2$ on ordered, clean, terraced surfaces of 6H-SiC. Epitaxial $CoSi_2$ with (111) orientation has been achieved where the $CoSi_2$ nucleation is controlled with a layered template structure. The epitaxial $CoSi_2$ film was formed on a hydrogen etched 6H-SiC(0001)$_{Si}$ surface by co-deposition of Co and Si at 550 °C.

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