TiC nanoisland formation on $6H-SiC(0001)_{Si}$

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TiC nanoisland formation on 6H–SiC(0001)_{Si}

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Spontaneous formation of titanium carbide nanoislands on silicon carbide substrates has been studied with scanning tunneling microscopy and x-ray absorption near-edge spectroscopy. Scratch-free and atomically flat 6H-SiC(0001)_{Si} substrates were prepared by high temperature hydrogen etching. The surfaces were subsequently cleaned by *in situ* ultrahigh vacuum annealing. Titanium carbide nanoislands were formed by titanium deposition and annealing at 950 °C. The average width (10–50 nm) and separation of the Ti islands was controlled by varying the titanium coverage (0.1–0.3 nm) and the annealing time (1–20 min). At the lowest coverage, the islands were uniformly distributed over the surface, while at higher coverage the islands tended to collect at the substrate step edges. © 2002 American Institute of Physics. [DOI: 10.1063/1.1465121]

I. INTRODUCTION

The fabrication of artificial, low-dimensional structures such as nanoislands on semiconductors has attracted much attention due to the continued miniaturization and anticipation of novel electronic devices. Recently, several efforts have been made to prepare clusters,¹ quantum dots,² quantum³ and nanowires,^{4–6} single-electron transistors (SET),^{7.8} and quantum-dot lasers.⁹

A variety of metal and semiconductor materials have been used, and Si dots^{10,11} as well as Si/Ge (Ref. 12) nanocrystals on SiC substrates have been investigated, but minimal data exist concerning metal carbide nanostructures on H_2 etched SiC substrates.

Silicon carbide is a refractory semiconducting material with promising substrate properties for nanostructures. The material has a wide band gap of 3.03 eV (6H–SiC), which makes it attractive for SET's. More charging states can be confined at the nanoisland/semiconductor junction by means of deposition of a metal with a large Schottky barrier height (SBH) to SiC such as titanium (0.73-1.09 eV).¹³ In addition, an ordered substrate surface can be prepared on SiC by hydrogen etching providing a foundation for nanostructure growth such as quantum wires. Hydrogen etching of 6H–SiC results in an array of terraces with evenly spaced single unit cell height steps (~1.5 nm) with straight edges.^{14–16}

Since titanium reacts with both Si and C, then titanium carbides, titanium silicides, and mixed alloys are possible through interface reactions of Ti on 6H–SiC substrates. Titanium carbide is a potentially interesting compound material for nanotechnology because it has a high oxidation resistance,¹⁷ and it forms a low resistivity ohmic contact to SiC.¹⁸ In a previous study of titanium disilicide nanoislands on Si(001) surfaces,¹⁹ it was argued that for a large lattice

mismatch spontaneous island growth will occur, and that this can lead to a stable distribution of island sizes. Both the C54 phase of TiSi₂ and 6H–SiC have hexagonal crystal structures and a lattice mismatch of 10.7%. TiC is cubic, but has a much smaller in-plane mismatch of 0.6% to 6H–SiC {that between $(111)_{TiC}$ and $(0001)_{SiC}$ }^{20,21} However, in the present work, it is demonstrated that spontaneous TiC nanoisland formation on 6H–SiC(0001) can be achieved.

II. EXPERIMENT

The TiC nanoislands were formed within an ultrahigh vacuum (UHV) deposition and analysis system, that operates at a base pressure in the high 10^{-11} Torr range and is equipped with facilities for molecular—beam epitaxy, scanning tunneling microscopy (STM), and low-energy electron diffraction (LEED).

As supplied on axis, *n*-type $6H-SiC(0001)_{Si}$, wafers from CREE Research Inc. were first ex situ cleaned with a HF:H₂O(10:1) solution and subsequently treated with atmospheric hydrogen in a H₂ etching system at 1600 °C for 20 min. A tungsten film was then sputtered onto the back side of each wafer to facilitate in situ heating by absorption of infrared radiation. Immediately after an exposure to UV/ozone irradiation and another chemical cleaning with a HF:H₂O:ethanol (1:1:10) solution, the wafers were loaded into the UHV system. After overnight degassing at room temperature, the SiC samples were heat treated at 1040 °C for 10 min. The sample temperature was measured with an optical pyrometer. After cooling down to room temperature, titanium (0.1-0.3 nm) was deposited and subsequently annealed at 950 °C for 1-20 min. The Ti was deposited in UHV with an electron-beam source. The deposition rate was established with a quartz crystal monitor, and the deposited thicknesses were obtained by timed opening of a shutter between the source and substrate.

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FIG. 1. STM image of hydrogen etched 6H-SiC(0001)_{Si} surface. The scan size is $2 \times 2 \ \mu m^2$ and the black-to-white scale is 1.9 nm.

STM observations were carried out after each UHV surface preparation step using a Park Scientific VP instrument with a tungsten tip. The samples were also studied *ex situ* with x-ray absorption near-edge spectroscopy (XANES) and atomic force microscopy (AFM). The Ti *K*-edge XANES 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. Energy calibration was set to 4966 eV at the Ti foil *K*-edge inflection point. AFM data was acquired in contact mode with a Park Scientific Autoprobe M5 instrument. The typical radius of curvature of the silicon nitride tips is reported by the manufacturer to be ~10 nm.

III. RESULTS AND DISCUSSION

The surface morphology of a H₂ etched and heat treated $6H-SiC(0001)_{Si}$ sample is shown in the STM image in Fig. 1. The original surface shows polish-induced scratches while the hydrogen etching removes of both Si and C from the SiC surface and leaves single unit cell steps and terraces.¹⁴⁻¹⁶ The terraces are about 600 nm in width and separated by straight steps that are one 6H unit cell high (1.5 nm). The terraces appeared to be uniformly distributed across the sample surface. Similar stepped surface morphologies for H₂ etched $6H-SiC(0001)_{Si}$ were also observed by Mårtenson *et al.*,¹⁴ Ramachandran *et al.*,¹⁵ and Xue *et al.*¹⁶ The terraces appeared to be atomically flat and, therefore, are ideally suited for nanoisland formation studies. LEED measurements of these samples revealed a ($\sqrt{3} \times \sqrt{3}$) surface reconstruction in agreement with previous studies.^{14,22}

Starting from the stepped substrate, a 0.3 nm Ti film was deposited and annealed at 950 °C for 1 min. As shown by the STM image in Fig. 2(a), the ultrathin film covered the terraces homogeneously without forming islands or agglomerating at the steps. However, annealing for an additional 19 min at the same temperature caused the film to form nanoislands, which were measured to be 30–50 nm in width and about 2.5 nm in height. A line scan is displayed in the image to more clearly present the dimensions of the islands. There was neither evidence of ordering of the islands into an array,



FIG. 2. STM images of 0.3 nm Ti on 6H–SiC(0001)_{Si} annealed at 950 °C for (a) 1 min and (b) 20 min. The scan sizes are 0.5×0.5 and $0.3 \times 0.3 \ \mu m^2$, and black-to-white scales are 2.1 nm and 2.8 nm, respectively. The white line in (b) corresponds to the location of the line scan presented in (c). Note that the vertical scale is enhanced in (c).

nor was there a distinct separation between the islands. However, the islands seemed to form preferably toward the step edges of the 6H-SiC(0001)_{Si} substrate.

The nanoislands were investigated using *ex situ* XANES. The data from the nanoislands as well as standard spectra for TiC, TiO₂, Ti₅Si₃, C54 TiSi₂, and Ti metal are shown in Fig. 3. The two TiSi₂ phases (C49 and C54) are indistinguishable in XANES and therefore only the C54 phase is displayed in Fig. 3. From other studies^{23,24} of the interface reaction between Ti and 6H–SiC(0001)_{Si} it is known that Ti₅Si₃ and TiC form during annealing at 700 °C–900 °C. The TiC layer is observed to form at the SiC interface, which



FIG. 3. Normalized XANES data for (a) 0.3 nm Ti/6H–SiC(0001)_{Si} annealed at 950 °C for 20 min, (b) TiC, (c) TiO₂, (d) Ti₅Si₃, (e) C54 TiSi₂, and (f) Ti foil.



FIG. 4. (a) STM image (error signal) and (b) AFM image of 0.1 nm Ti on $6H-SiC(0001)_{Si}$ annealed at 950 °C for 20 min. The scan sizes are 0.3×0.3 and $1.4 \times 1.4 \ \mu m^2$, respectively. The black-to-white scale in (b) is 2.6 nm. The white line in (a) corresponds to the location of the line scan presented in (c). Note that the vertical scale is enhanced in (c).

may be attributed to the lower free energy of formation.²³ A careful inspection of the XANES spectra in Fig. 3 shows that the nanoislands display the same features as the TiC reference sample indicating that Ti consumed C from the SiC substrate and transformed into TiC during the annealing at 950 °C for 20 min, which is in agreement with the previous studies of the reaction of Ti films on 6H-SiC.^{23,24} The measurements do not identify the presence of excess Si. Based on the prior studies, it is expected that the TiC will form near the SiC interface,^{23,24} and the Si will accumulate at the surface of the TiC islands. A common method of preparing clean SiC surfaces involves deposition of excess Si while annealing at 900 °C.14 The excess Si evaporates or desorbs from the surfaces leading to the formation of a $(\sqrt{3} \times \sqrt{3})$ surface reconstruction.¹⁴ We may expect similar evaporation of excess Si from a TiC surface. It is, therefore, likely that during the process of TiC nanoisland formation, the excess Si surface atoms migrate to the island surface or segregate into Ti-silicide islands. The extended annealing then results in the evaporation of the Si.

To explore whether the island separation and size could be controlled, a lower Ti coverage of 0.1 nm was deposited on a H₂ etched/heat treated $6H-SiC(0001)_{Si}$ substrate. Island formation was induced through annealing at 950 °C for 20 min. The STM error signal image of the resulting nanoislands is shown in Fig. 4(a). The error signal is proportional to the derivative of the actual scan and is shown here for the sake of improved visualization. The TiC nanoislands are $\sim 1-3$ nm high, 10–20 nm wide, separated by $\sim 15-20$ nm, and homogeneously distributed across the SiC terraces. This random arrangement of the Ti islands across the ordered SiC surface is also evidenced by the AFM image in Fig. 4(b). In particular, there was no evidence of preferred formation along the step edges for this coverage.

We consider now the mechanism for the formation of TiC nanoislands on a SiC surface. As noted herein, the lattice mismatch between TiC(111) and SiC(0001) is small (0.6%).

However, if the film has a high surface energy in comparison to the substrate, island formation will occur independent of the magnitude of the mismatch.²⁵ The surface energy of SiC $(\gamma_{SiC} = 840 \text{ erg/cm}^2 \text{ at } 1200 \text{ °C})^{26}$ is a factor of two less than that of TiC $(\gamma_{TiC} = 1930 \text{ erg/cm}^2 \text{ at } 1100 \text{ °C}).^{27}$ We propose that the difference in surface energies is the driving force for TiC nanoislands formation on SiC substrates. We note that the islands exhibit similar relative dimensions for the 0.1 and 0.3 nm Ti depositions. These results again support the proposal that the island formation is driven by energetics while the kinetics may be important in the determination of the average island size. The apparently preferred formation of TiC islands (for the 0.3 nm Ti) near the SiC step edges may also involve an interplay of both the kinetics and energetics of the system, however, more research is necessary to describe this phenomena. The high temperature (\sim 950 °C) contributes to both the interface reactions and to diffusion to minimize the surface energy. For nanoisland formation, the surface energies may not be sufficient to describe the energetics. For instance, it is known that the surface energy changes with island size, and for small crystals (1-10 nm in dimension), quantum-mechanical effects and impurities may significantly alter the various physical properties.²⁸

IV. CONCLUSIONS

The formation of TiC nanoislands on H₂ etched and heat treated 6H-SiC(0001)Si substrates was studied. The XANES data indicated that the Ti reacted with the SiC and spontaneously formed nanoislands consisted of TiC. It is proposed that the excess Si evaporates from the surface during the formation process. The island formation process appears to be driven by the large surface energy of TiC, and the low interface energy of TiC and SiC may lead to the preference of TiC over Ti silicides. TiC has a demonstrated high resistance to oxidation,¹⁷ which means that the metal nanoislands can be removed from the vacuum system for technological applications such as single-electron devices or contacts to molecular structures. A next step would be to take advantage of the ordered SiC terraced surface, which is adjustable through miscut, and to produce TiC nanowires through surface diffusion and bonding at the step edges.

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