Oxidation at Cs Pre-Adsorbed Si/6H-SiC(0001)-(3 × 3) Reconstructed Surfaces Studied Using Metastable-Induced Electron Spectroscopy*

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A Si-covered 6H-SiC(0001) surface was transformed from a Si-rich to C-rich one with increasing annealing temperature. An alkali metal is well known for promoting oxidation. We studied the oxidation to Cs pre-adsorption on a 6H-SiC(0001)-(3 × 3) reconstructed surface using metastable-induced electron spectroscopy (MIES), ultraviolet photoelectron spectroscopy (UPS), and low-energy electron diffraction (LEED). The (3 × 3) reconstructed surfaces was adsorbed Cs and exposed oxygen at room temperature. The MIES results show that the intensity of electron emission induced Cs6s increased with Cs evaporation. For the oxygen-exposed Cs/SiC surface, the emission intensity of the Cs6s-induced peak rapidly decreased and a dissociated adsorption oxygen-induced peak appeared. When the oxygen-adsorbed Cs/SiC(0001) surface was annealed until 800°C, Cs atoms were desorbed from the surface and O bonded with Si, forming SiO₂.

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I. INTRODUCTION

SiC has superior properties for electric device applications in extreme environments such as those with high temperature, high voltage, high frequency, and high power. Knowledge of the electronic structure and formation of the insulating film is very important for its application to SiC devices. A high-quality SiO₂ insulating film was fabricated on a SiC surface using a wet and dry oxidation method [1]. However, interface traps were generated at the SiO₂/SiC interface, which is a disadvantage. The interface traps resulted in reduction of the channel mobility in the SiC metal-oxide-semiconductor field effect transistor (MOSFET) [2, 3]. The Si-covered 6H-SiC(0001) surface was transformed from a Si-rich to C-rich one such as (3 × 3), ($\sqrt{3} \times \sqrt{3}$)R30°, and ($6\sqrt{3} \times 6\sqrt{3}$)R30° surfaces owing to the desorption of Si atoms from the SiC surface with increasing annealing temperature [4–6]. During oxidation of the (3 × 3) reconstructed surface on the Si predeposited 6H-SiC(0001) surface, oxidation layers were formed at low temperature (500°C) and low oxygen exposures (1000 L) on the SiO₂/SiC interface [7]. Oxidation at the ($\sqrt{3} \times \sqrt{3}$)R30° reconstructed surface using N₂O gas with sample annealing was studied using high-resolution photoemission spectroscopy [3]. Alkali metal is a well-known catalyst used to promote oxidation. At the Cs pre-adsorbed Si(100) surface, SiO₂ is easily formed

on the Si surface with small amounts of oxygen exposure [8, 9]. The reduction of the interface traps has been reported with Na-enhanced oxidation of a Si-face 4H-SiC surface [2].

We studied the oxidation to Cs pre-adsorption on a 6H-SiC(0001) reconstructed surface using metastable-induced electron spectroscopy (MIES), ultraviolet photoelectron spectroscopy (UPS), and low-energy electron diffraction (LEED).

II. EXPERIMENTAL

The measurement chamber was equipped with a helium metastable atom (He*) source, LEED optics, Si evaporator, and retarding-field energy analyzer. Helium atoms were excited to the metastable state using hot-cathode low-voltage discharge, as a result of which photons ($h\nu = 21.2$ eV) and He* were produced. These particles were separated by an electrical procedure owing their time-of-flight difference. We obtained the electronic structure of each using MIES and UPS on the same surface. He* atoms are de-excited at the surface through several processes such as Auger de-excitation (AD) and resonance ionization followed by Auger neutralization (RI+AN) depending on the surface work function [10]. The electron spectrum for the AD process directly reflects the local density of states at the de-excited position of the He* atoms. The spectrum for the AN process exhibits self-convolution of a local DOS. The change of the work function ($\Delta\Phi$) was estimated from the low-energy thresholds of the spectra obtained using UPS.

The sample is a *n*-type 6H-SiC(0001) substrate (Mateck) cleaned in vacuum using direct-current Joule

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FIG. 1. Spectra obtained using MIES for the 6H-SiC(0001)-(3×3) surface (open circles): (a) Simulation of self-convolution of the 3s partial DOS. (b) Convolution of the 3s partial DOS and the 3p partial DOS. (c) Self-convolution of 3p partial DOS. The combination of curves (a), (b), and (c) is represented by the black line.

heating (900°C, 1 min). The sample's temperatures were recorded using an infrared pyrometer. In order to achieve surface reconstruction, Si atoms were deposited on the SiC surface by annealing the Si(100) substrate at more than 1000°C. The (3×3) structure at the Si/6H-SiC(0001) surface was reconstructed by annealing the sample at around 850°C, and was observed using LEED. Cs was deposited using a carefully degassed dispenser from SAES Getters. Oxygen gas was exposed up to 30 L (1 L = 10⁻⁶ Torr·s) at room temperature.

III. RESULTS AND DISCUSSIONS

A. De-excitation of He* atoms at the 6H-SiC(0001)-(3×3) surface

Figure 1 shows the spectrum obtained via MIES for the 6H-SiC(0001)-(3×3) surface. For simulating the observed spectrum, several kinds of convolutions were evaluated using the published data for the partial density of states (DOS) for Si atoms calculated by L. I. Johansson *et al.* [11]. Curve (a) in Fig. 1 is a self-convolution of the 3s partial DOS. Curve (b) is a convolution of the 3s partial DOS and the 3p-partial DOS. Curve (c) is a self-convolution of the 3p partial DOS. The convolution of Si 3s × 3p results in a main peak (P₁) around 7 eV in the measured spectrum. The shoulder structure P₂ is reflected in curve (b) and is the peak of the self-convolution of 3p. Therefore, the spectrum of the (3×3) surface does not directly reflect the partial DOS of the Si atoms. This result suggests that He* is dominantly de-excited through the RI+AN process at the (3×3) surface.

FIG. 2. Spectra obtained using MIES for the Cs/SiC(0001) surface: (a) 6H-SiC(0001)-(3×3) surface, (b1–b6) Cs deposited SiC surfaces until 900 s.

B. Cs adsorption at the 6H-SiC(0001)-(3×3) surface

We obtained spectra of the Cs deposited 6H-SiC(0001)-(3×3) surface up to 900 s at room temperature using MIES. Figure 2 shows the spectra in the course of Cs adsorption on a 6H-SiC(0001)-(3×3) surface. Figure 3 shows the $\Delta\Phi$ between the clean SiC surface and each Cs adsorbed surface. The shoulder structure in the low-energy region in Fig. 2, S₁, is due to electron emission

FIG. 3. Intensity variations of the Cs 6s induced peak (closed circles) and work function change (squares) as functions of the Cs deposition time.

FIG. 4. Spectra obtained using MIES for the oxygen exposed Cs/SiC(0001) surface: (b6) Cs/SiC(0001) surface, (c1–c6) Cs/SiC surfaces with oxygen exposures up to 30 L.

from the spin-orbit splitted Cs 5*p* induced states. The peak around 15.1 eV, P₃, appeared with Cs deposition time more than 60 s. This peak is due to emission from the Cs 6*s* induced states through the AD process. During the initial Cs deposition (b1–b2 in Fig. 2), the intensity of S₁ increased. However, the Cs 6*s* peak did not appear. It is possible that the electrons of Cs 6*s* were transferred to the SiC substrate. The work function drastically decreased in the initial deposition region in Fig. 3. This result indicates that a dipole was formed between the Cs and SiC surface. During the Cs deposition time from 60 to 120 s (b3–b4), the intensity of P₃ slightly increased. We found from the change of work function that the electrons of Cs transferred to Si on the surface were filled at 120 s Cs deposition time. With increasing Cs deposition time, the intensity of the Cs 6*s* and Cs 5*p* peaks increased. The $\Delta\Phi$ value was almost constant at -1.2 eV after 200 s of deposition time. These results imply that the Cs bonding may change to a metallic bond around this deposition time. From 420 to 900 s (b5–b6), the intensity of P₃ did not change. This indicates that Cs was saturated on the surface. However, the peak and shoulder structure for Si did not disappear. If the surface was completely covered with Cs, He* could not interact with the Si atoms.

C. Oxygen adsorption at the Cs/6H-SiC(0001)-(3 × 3) surface

Figure 4 shows spectra obtained using MIES of the Cs saturation adsorbed 6H-SiC(0001) surface (Fig. 2 (b6))

FIG. 5. Intensity variations of the Cs 6*s* induced peak (closed circles) and work function change (square) as functions of the oxygen exposure.

FIG. 6. Spectra obtained using MIES for the O/Cs/SiC(0001) surface: (c6) O/Cs/SiC(0001) surface, (d1–d4) O/Cs/SiC surfaces annealed at temperatures up to 800 °C.

with increasing oxygen exposure up to 30 L. The corresponding $\Delta\Phi$ values at the same surface are shown Fig. 5. During the initial oxidation (c1–c3), the intensity of P₃ decreased rapidly, and S₂ appeared and was slightly shifted to a lower energy. The shoulder structure S₁ contains a peak due to electron emission from the O 2*p* induced states. Here, the work function increased drastically. It was 0 eV for oxygen exposure greater than 4 L. O₂ molecule was dissociatively adsorbed on the surface by the catalytic reaction of Cs 6*s* electron. Therefore, Cs promoted surface oxidation. At high oxygen exposures (c4–c6), the spectra were almost the same. The intensity

of Cs 5*p* did not change during oxygen exposure. This means that dissociated O atoms adsorbed beside Cs atom.

The spectra for the oxygen-adsorbed Cs/SiC(0001) surface (Fig. 4 (c6)) with annealing until 800°C are shown in Fig. 6. When the temperature is 500°C, S_1 decreased and the O 2*p* induced state (P_4) shifted to a low energy. Hence, the adsorbed Cs atoms were desorbed from the surface. At 800°C, S_1 disappeared and the Si–O bonding peak (labeled P_4) appeared around 7.2 eV, as shown in Fig. 6(d4). Therefore, Cs atoms were removed from the O/Cs/SiC surface, and SiC was oxidized to SiO₂. However, in another study, the MIES results show that the intensity of the O 2*p* induced peak is less than that of SiO₂ [8, 12]. This may have been due to the development of a SiO_x surface such as SiO₂. Another researcher reported that the oxidation of the 4H-SiC(0001)-(3 × 3) surface was similar to that of the Si(111)-(7 × 7) surface [13]. The oxidation of the (7 × 7) surface results in the formation of Si adatoms and trimers. Our results show that initial oxidation is possible for local Si atoms such as Si

tetramers and Si adatoms on the Cs desorbed surface.

IV. CONCLUSIONS

We studied the oxidation to Cs pre-adsorption on 6H-SiC(0001)-(3 × 3) reconstructed surface using MIES, UPS, and LEED. During the initial Cs deposition, the work function drastically decreased, and electrons of the adsorbed Cs6*s* were transferred to the SiC substrate. It is possible that Cs atoms formed metallic bonds on surfaces with high amounts of Cs deposition. At the oxygen-exposed Cs/SiC-(3 × 3) surface, the work function was increased to ~ 0 eV for small amounts of oxygen exposure. The oxygen atom was dissociative adsorption by the catalytic reaction of the Cs 6*s* electron. We observed that Cs promoted oxidation at room temperature. The spectrum of the surface annealed at 800°C showed that in spite of Cs being desorbed, O atoms kept to adsorb on the SiC-(3 × 3) surface.

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