Characterization of the 6H-SiC(0001) surface and the interface with Ti layer with the Schottky limit

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Abstract

The Ti/6H-SiC(0001) interface with the Schottky limit and the SiC surfaces before metallization are investigated using low energy electron microscopy (LEED), Auger electron spectroscopy (AES), X-ray photoemission spectroscopy (XPS), scanning tunneling microscopy (STM), and cross-sectional transmission electron microscopy (TEM). The surface to form the resultant Schottky limit is prepared by dipping the SiC wafer into pure boiling water of $100\,^\circ\text{C}$ for 10 min. The surface has the $1\times1$ surface reconstruction with a small amount of oxygen less than 5%, suggesting that the surface is mainly terminated by hydrogen. In the STM analysis, we found that oxygen strongly terminates atomic step edges, which leads to the drastic reduction of the resultant density of interface states after metallization at room temperature. Epitaxial and commensurate relations between a Ti layer and the SiC substrate without any interface layer were found by cross-sectional TEM analysis. The observed commensurate interface indicates that the surface hydrogen terminator on the terraces was desorbed after metallization. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Control of the Schottky barrier height at the metal/semiconductor interface is one of most important issues in semiconductor physics and electronic device applications. Many efforts on Schottky barriers have been devoted to metal/Si and metal/GaAs interfaces because of their wide device applications and their accumulated scientific knowledge. It has been found that these interfaces have large amounts of interface states to let the interface Fermi level pin at an energy level in the band gap, thereby forming constant barrier heights insensitive to changing the metal and semiconductor surface preparations [1,2]. The pinning degree is expressed by the slope parameter $S^\phi = \phi_b/\phi_m$, where $\phi_b$ is the Schottky barrier height and $\phi_m$ is the metal work function. When $S^\phi = 1$ (the Schottky limit), there is no interface states and $\phi_b$ changes with the change of $\phi_m$. When $S^\phi = 0$ (the Bardeen limit), $\phi_b$ is constant with a high density of interface states. Practical semiconductors have been believed to have their own $S^\phi$ factors depending on their ionicity [3,4]. Typical estimated $S^\phi$ values for Si and GaAs were $\sim 0.02$.

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and 0.14 [5], respectively, which are much lower than unity of the Schottky limit because of their small ionicities.

Even in these heavily pinned semiconductors, there were some important reports on the wide control of $\phi_b$. Pb deposition on hydrogen-terminated $n$ and $p$-Si(111) surfaces prepared by buffered HF solution dipping [6], an Hg contact on a hydrogen-terminated $p$-Si(111) surface [7], metal depositions at 90 K on the $n$-GaAs(001) surface [8] were reported to achieve wide variations of $\phi_b$, which implied the Schottky limit. In wide band-gap semiconductors whose research has become popular and extensive recently their higher $S$ factors or weaker pinning degrees are significant advantages superior to the smaller gap semiconductors in controlling the barrier height. Recently, we have reported that barrier heights at metal/6H-SiC(0001) interfaces indicate the Schottky limit and the barrier heights were controlled widely by changing surface preparation methods before metallization [9]. Understanding the origin of the electrical ideality in terms of atomic structure is necessary to know information on the guideline to control the Schottky barrier. In this paper, we investigate the SiC surfaces by low energy electron microscopy (LEED), Auger electron spectroscopy (AES), X-ray photoemission spectroscopy (XPS), and scanning tunneling microscopy (STM). Further, the Ti/6H-SiC(0001) interface was observed by cross-sectional transmission electron microscopy (TEM).

2. Experiment

Commercially available nitrogen-doped n-type 6H-SiC (0001) epitaxial wafers with 1° diameter and 3.5° tilt toward the [1120] direction were used in this study. Samples cut into $12 \times 3 \text{ mm}^2$ were degreased followed by Piranha solution ($H_2SO_4:H_2O_2 = 4:1$ at 120°C) to remove organic contamination. After rinsing the samples by pure water, they were cleaned by RCA SC-1 and SC-2 procedures. Some of the samples were thermally oxidized in a quartz tube furnace at 1100°C for 150 min using dry oxygen gas. The thickness of the oxidized layer was 10 nm. The oxidized layer was etched by dipping in 5% HF solution. We will abbreviate this treatment of oxidation followed by dipped into 5% HF solution as O/E treatment hereafter. Some of O/E treated samples were immersed in boiling water at $\sim 98$°C or higher for 10 min. This treatment will be abbreviated as BW treatment. It is known that a Si(111) surface dipped into boiling water with dissolved oxygen (DO) of $<10$ ppb is monohydride terminated [10]. In this experiment, pure water with a DO density less than 3 ppm was used. Resistivity of the water was 18.2 MΩ cm and the concentration of total organic carbon (TOC) was around $<10$ ppb. All samples were rinsed in the deionized pure water and blown by particle-free N$_2$ gasses after each surface treatment. The density of particles with the diameter $\geq 0.3$ μm in our experimental room was about $5 \times 10^3$ particles/ft$^3$ that was around one tenth lower than outside. The room temperature was set at $26 \pm 0.1$°C and the typical relative humidity was about 40%.

The samples were loaded into a hand-made designed surface analysis system soon after finishing the final chemical procedure. For comparison, one sample was loaded into the chamber after leaving it in the atmosphere of the experimental room for few days. The analyzing system was fabricated by a special treatment. The stainless-steel SUS316L chambers were heat treated at 1080°C in a vacuum to remove residual hydrogen in the steel before system assembly, which are evacuated only by high-performance turbo molecular pumps (Osaka Vacuum TG-1121M) with the base chamber pressure of lower than $1 \times 10^{-11}$ Torr. The vacuum is measured by extractor gauges (Leybold IONIVAC IM520). The electron analyzer is commercial hemi-spherical type VG-CLAM2. The detection angle was set normal to the sample surface. The X-ray source used for an XPS analysis was a Mg target with photon energy of 1253.6 eV. The electron energy in AES analysis was 5 keV. The electron gun was set at the angle of 60° from the surface normal. The LEED system is rear-view type VG RVL-900.

In an STM analysis, the boiling water procedure was performed in nitrogen atmosphere formed in a hand-made glove box with an oxygen density less than 2 ppm and with zero particle count for $\geq 0.1$ μm. The chemically prepared sample with the size of $3 \times 10 \text{ mm}^2$ was loaded into the STM system using a stainless-steel transfer box that can be con-
nected directly to the glove box and the STM system under the clean atmosphere. The base pressure of the STM system modified from UNISOKU USM-501 is \( \sim 2 \times 10^{-11} \) Torr.

In a TEM analysis in this report, JEOL JEM-4000EX system with an electron acceleration voltage of 300 keV was used. The TEM analysis was done for a 5% HF-treated sample and a BW sample. Ti was evaporated on the samples at room temperature after outgassing from the samples at 200°C in a hand-made electron beam evaporator with the base pressure of \( \sim 2 \times 10^{-11} \) Torr. The maximum pressure during the Ti evaporation was 2 \( \times 10^{-9} \) Torr. The Ti/6H-SiC(0001) samples were thinned by an Ar ion milling system so as to observe the cross-section of the interface. The direction of the electron transmission was the \langle 11\bar{2}0 \rangle \) axis.

3. Results and discussion

On the 5% HF-treated sample, no spot was observed in the LEED analysis indicating a disordered surface. Sharp \( 1 \times 1 \) spots were observed on the O/E-treated and the BW-treated sample. This suggests that the disordered surface layer was removed by O/E treatment.

Fig. 1 is an AES survey scan on the BW surface quickly loaded to the chamber soon, showing a small amount of oxygen and indicating the main constituent elements on the surface are Si and C atoms. The ratio of oxygen atoms on the surface, which is estimated from the peak-to-peak ratio of the three peaks divided by the relative sensitivities, is less than 5%. From XPS measurements, we have also observed the small amount of oxygen on the BW surface with 9% peak height ratio of O 1s/Si 2p. On the BW sample left in the atmosphere a few days showed a large oxygen amount of 75%. This indicates that the oxygen concentration on the surface increases with increasing the time of exposing it to the air.

A detailed Si LVV AES peak shape on the BW sample (E) is depicted in Fig. 2 with reference spectra from the Si(111)-7 \times 7 \) surface (A) [11], the 6H-SiC(0001)-3 \times 3 \) surface (B) [12], the 6H-SiC(0001)-\( \sqrt{3} \times \sqrt{3} \) surface (C) [12], and the oxygen-adsorbed 6H-SiC(0001)-\( \sqrt{3} \times \sqrt{3} \) surface (D) [13]. The most prominent peak at 92 eV on the Si(111) surface (A) is also observed in (B) and (C) as their main peaks at slightly shifted energy positions, whereas in (D) and (E), the peak shifted widely to 85–86 eV. Thus, the 3 \times 3 and \( \sqrt{3} \times \sqrt{3} \) surfaces have similar valence band feature to the Si crystal surface at least in observation from the Auger process and the \( \sqrt{3} \times \sqrt{3} \) and 1 \times 1 BW surfaces have a significantly different valence band feature from the Si surface. The satellite peaks from 80 to 89 eV on (A) are observed also on the 3 \times 3 surface and the \( \sqrt{3} \times \sqrt{3} \) surface, which is consistent with the presence of Si–Si bond. This is consistent with structural models of the 3 \times 3 and \( \sqrt{3} \times \sqrt{3} \) reconstructions. The 3 \times 3 reconstruction has been reported to have a large amount of extra Si on the first SiC substrate bilayer [14] and the \( \sqrt{3} \times \sqrt{3} \) reconstruction is believed to have a \( T \)–site Si adatom model [15]. Here, note that (A), (B), and (C) surfaces have reconstructions with dangling bonds. Since the \( \sqrt{3} \times \sqrt{3} \) surface still should have the Si–Si bond, the lack of the Si-related peaks on the \( \sqrt{3} \times \sqrt{3} \) surface strongly suggests that the lack is derived from the presence of oxygen or the passivation (dangling bond termination) itself. Further, the \( \sqrt{3} \times \sqrt{3} \) and 1 \times 1 BW surfaces have the main peak at almost the same 85 to 86 eV while the 1 \times 1 BW surface
have little oxygen on the surface. This implies that the difference between the (A)–(C) group and (D)–(E) group is derived from the passivation of the dangling bonds on (D) and (E). Since the main area of the surface is passivated by the terminator except oxygen and the detected atoms in the AES and XPS analyses were Si, C, and O atoms, we infer that the possible terminator is a hydrogen atom.

In our STM analysis, we observed that no atomic image from the BW surface annealed below 400°C. This is probably because of stronger water adsorption onto the ionic surface. After annealing at 970°C, atomic images were observed as shown in Fig. 3. The surface in Fig. 3a has atomic steps of 2.5 nm height corresponding to a bilayer. And the average width of the step edges in the [11\(\overline{2}0\)] direction is around 5 nm, which is consistent with the macroscopic off-angle of 3.5° in the [11\(\overline{2}0\)] direction. This indicates that the surface has the regular step structure with no undulation everywhere on the surface. The steps tend to have a zigzag shape with the edge directions along the [1\(\overline{2}10\)] and [2\(\overline{1}\)10] directions, which is consistent with an STM analysis of 6H-SiC(0001)-6\(\times\)6 surface [16]. The important finding from the STM analysis was adsorbates at the step edges appeared as white protrusions. The protrusion is a stable structure because the surface has been
annealed at 970°C. In Fig. 3b, the adsorbates are clearly found at the edges while the terraces have a periodical atomic arrangement that has been found to be the $\sqrt{3} \times \sqrt{3}$ reconstruction as shown in the inset. We found that the BW surface exhibits the $\sqrt{3} \times \sqrt{3}$ pattern also in a LEED analysis after the same annealing at 970°C. In an AES analysis after annealing, the residual oxygen was still observed with around one half amount of that before the annealing. Thus, the protrusions are oxygen strongly chemisorbed at the step edges. Although the detailed bonding structure is unknown so far, it is obvious that the BW surface is strongly passivated at the step edges by the small amount of oxygen chemisorbed preferentially. Since $1 \times 10^{13}$ states/cm$^2$/eV is enough for the perfect pinning (the Bardeen limit) [17], the step edge passivation plays a significant role in the reduction of interface states when the interface and the semiconductor surface prepared are completely terminated in the terrace area.

In the cross-sectional TEM observations of Ti/6H-SiC(0001) interfaces prepared by 5% HF treatment and BW treatment, we found a prominent difference in interface abruptness between them. Fig. 4a is a TEM micrograph of the interface prepared by 5% HF treatment. The image was observed along the [1120] direction. The SiC crystal for the TEM observation was a substrate with zero mis-cut angle. The titanium layer on the 6H-SiC(0001) substrate was assigned to the fcc type from the TED pattern. There are many dislocations in the Ti layer and a disordered interfacial layer between the Ti and the 6H-SiC crystal. The thickness of the disordered layer is about 2 nm. Even in the disordered layer the lattice is not amorphous but distinctive, suggesting that the degree of disorder is relatively small. In the other micrograph of the interface prepared by BW treatment in Fig. 4b, there is no disordered layer and the interface is abrupt. The interface position was determined as the position where the periodical 6H-SiC lattice ends. The fcc-Ti layer is epitaxially grown on the 6H-SiC(0001) substrate.

It is known that typical Ti crystal structures are 2H and body-centered cubic. Porter et al. [18] reported that the Ti structure on the 6H-SiC(0001) substrate whose surface was prepared by diluted HF dipping was 2H type. This crystal ($a = 0.29505$ nm) has a 4.3% lattice mismatch with the 6H-SiC(0001) crystal ($a = 0.3.0806$ nm). In the BW surface, however, the structure is the fcc-Ti, having a significantly small misfit parameter of 0.79% between the $\{111\}_\text{fcc-Ti}$ and $\{112\}_\text{6H-SiC}$ faces [19]. The resultant interface is commensurate without an edge dislocation along the interface normal. This structure transformation to form the commensurate interface evidences the direct bonding between the two layers without any terminator that was present on the SiC surface before the Ti deposition. Otherwise, the interface would have the 2H-Ti lattice at the interface as reported by Porter et al. Thus, the terminator atoms desorbed during the Ti deposition. The chemisorbed oxygen at the step edges may have a

Fig. 4. Cross-sectional TEM images of the Ti/6H-SiC(0001) interfaces prepared by (a) 5 HF dipping treatment and (b) BW (boiling water dipping) treatment as the surface cleaning methods for the 6H-SiC substrate. It is clearly observed that image (a) has a disordered interface layer with the thickness of $\sim 2$ nm while an abrupt interface is observed in image (b). The interface is depicted by white dashed lines.
strong obstacle to the formation of an interface layer triggered from the step edges.

4. Conclusions

The 6H-SiC(0001) surfaces prepared by boiling water dipping and the interface formed by the Ti layer deposition on the surface were investigated. The 6H-SiC(0001) surface prepared by the boiling water dipping has the $1 \times 1$ reconstruction with around 5% concentration of oxygen atoms that are chemisorbed preferentially at the step edges on the surface. The Ti/6H-SiC(0001) interface is commensurate, which indicates the direct bonding between Ti and Si layers without any terminator that was present on the surface before the Ti deposition.

References

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