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Platinum-catalyzed hydrolysis etching of SiC in water: A density functional theory study

Pho Van Bui^{1*}, Daisetsu Toh¹, Ai Isohashi¹, Satoshi Matsuyama¹, Kouji Inagaki¹, Yasuhisa Sano¹, Kazuto Yamauchi^{1,2*}, and Yoshitada Morikawa^{1,2*}

¹Department of Precision Science and Technology, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan ²Research Center for Ultra-Precision Science and Technology, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

*E-mail: buivanpho@up.prec.eng.osaka-u.ac.jp; yamauchi@prec.eng.osaka.u.ac.jp; morikawa@prec.eng.osaka-u.ac.jp

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A comprehensive study of the physicochemical interactions and the reaction mechanism of SiC etching with water by Pt catalysts can reveal key details about the surface treatment and catalytic phenomena at interfaces. Therefore, density functional theory simulations were performed to study the kinetics of Pt-assisted water dissociation and breaking of a Si–C bond compared to the HF-assisted mechanism. These calculations carefully considered the elastic and chemical interaction energies at the Pt–SiC interface, activation barriers of Si–C bond dissociation, and the catalytic role of Pt. It was found that the Pt-catalyzed etching of SiC in water is initiated via hydrolysis reactions that break the topmost Si–C bonds. The activation barrier strongly depends on the elastic and chemical interactions. However, chemical interactions are a dominant factor and mainly contribute to the lowering of the activation barrier, resulting in an increased rate of reaction. © 2018 The Japan Society of Applied Physics

1. Introduction

Owing to its beneficial physical properties and high chemical stability, SiC is a promising semiconductor for use in high frequency, high power, and high efficiency devices.^{1,2)} In these devices, surface damage and the incomplete removal of contaminants can result in reduced device performance and vield.^{3,4)} Therefore, efforts have been made to understand the sources and nature of surface contaminants, and the damage caused during wet chemical surface etching and cleaning processes by conducting investigations into their detailed mechanism.^{5,6)} As SiC is extremely hard and inert, hydrofluoric acid (HF) is often used for etching and cleaning of its surface, particularly for the removal of native oxides and other contaminants.⁷⁻⁹⁾ The interactions between HF and Si surfaces as compared to that on SiC surfaces have been investigated in detail both experimentally and theoretically. The adsorption of F⁻ on Si of oxide surfaces induces a polarization of the Si-Si back bonds, which results in their weakening and allows etching of the oxide layer to take place. However, normal dipping into the HF solution in the case of SiC does not remove the last oxide layer on the topmost SiC surface, as evidenced in previous experimental observations that the surface instead ends up with OHterminations. However, SiC surfaces can be etched and effectively flattened by introducing a Pt catalyst, also known as the catalyst-referred etching (CARE) method in HF.^{10–14})

Recently, Isohashi et al.¹⁵⁾ have demonstrated that CARE using pure water with a Pt catalyst could planarize SiC to atomically smooth surfaces. The finding strongly indicated that even not using a corrosive HF as an etchant, SiC could be planarized via CARE in pure water. Using only pure water as an etchant, CARE is potentially applicable to planarization of many semiconductor surfaces, including GaN and oxides surfaces. Due to the potentials of CARE as a promising planarization method, many studies were carried out to understand its removal mechanism by extensively investigating the surface terminating species and mechanistic reaction pathways.^{11–14)} On the SiC surfaces processed via CARE in HF, high concentrations of F⁻ and OH⁻ terminations were experimentally observed. Using density functional theory (DFT) simulations, the origin of F⁻ terminations were verified to be a dissociative adsorption of HF onto the topmost Si-C bond assisted by the Pt catalyst. However, the formation of a large portion (over 40%) of OH-terminations has been experimentally observed on the surfaces planarized via CARE in HF. The exchange reaction between F⁻ and OH⁻ on the SiC(0001) surface was reported to be highly activated process⁷⁾ and therefore, the origin of the coterminations has not yet been clarified. The study by Isohashi et al. attempted to understand the mechanism and the differences between OH⁻ and F⁻ by comparing the material removal rate (MRR) of SiC etching via CARE under different conditions. A pressure of several kPa was applied on the backside of a SiC wafer to press the wafer onto a Pt surface. It is worth noting that the MRR strongly depends on the rotational speed and processing pressure.¹⁶⁾ However, our understanding of the interactive physicochemical phenomena occurring at the SiC-Pt interface in CARE is still limited owing to the difficulty in experimental examinations. For the same reasons, the detailed mechanism and differences between Pt-catalyzed etching phenomena of CARE in water and that in HF are also unclear. Thus, a comprehensive mechanistic understanding of these phenomena is potentially interesting in a variety of research fields, from mechanochemistry to industrial applications.

In order to achieve a molecular-level comprehension of the abovementioned phenomena, we investigated the mechanism of the first Si–C bond breakage via CARE with water and compared the results with that using HF by DFT simulations. Activation barriers for the proposed reaction pathways, the contribution of elastic and chemical interaction energies, and the catalytic roles of Pt have also been presented and discussed. These interaction energies were compared and evaluated as a function of the relative distance of Pt–SiC by elucidating the elastic and chemical contributions to the activation barriers.

2. Method and model

A slab model of SiC comprised of a stepped 3C-SiC(221) surface with a slab thickness of four Si(111) bilayers and Pt(111) layers is shown in Fig. 1. This model is similar to that



Fig. 1. (Color online) Ball-and-sticks model of 3C-SiC(221) and Pt(111) surfaces used in the simulations. The box shows a unit cell.

used in our previous study.¹⁴⁾ The surface structure of the SiC model matches the surface structure observed after CARE. Because of the similarities in the local atomic configurations and surface energies of 3C- and 4H-SiC, we expected that their calculated adsorption energies and activation barriers would also be similar. The Pt(111) surface mimics an experimentally observed Pt surface described in a previous study,¹⁷⁾ which reportedly has a high-intensity Pt(111) peak in its corresponding X-ray diffraction pattern. The stepped Pt(111) surface is used because of its high activity for water dissociation. Although the stepped Pt was modeled by three Pt layers, the calculated activation barrier of water monomer dissociation is consistent with the previous study.¹⁸⁾ (For more details, see Figs. S1 and S2 in the online supplementary data at http://stacks.iop.org/JJAP/57/055703/mmedia).

Successive slabs were separated by a vacuum region with a thickness of about 20 Å in the direction normal to the Pt(111) surface. The C atoms at the edge of the steps and dangling bonds in the bottom layers of the SiC model were terminated by H atoms. The topmost Si atoms were terminated by $OH^{-,19}$ The adsorbates, the two topmost bilayers of SiC (including their termination atoms), and the bottom layer of Pt were allowed to fully relax in the simulations. The remaining atoms were fixed in their ideal bulk positions in order to maintain the structures of the substrate and Pt(111).

Calculations were performed by using a first-principles approach with the STATE package, which has also been successfully applied in investigations of metals, semiconductors, and organic materials.^{14,19,20)} The first-principles simulations were based on the generalized gradient approximation with the Perdew–Burke–Ernzerhof functional.²¹⁾ In order to accurately calculate the activation barriers of the etching process, long-range dispersion correction scheme (rev-vdW-DF2) was employed.²²⁾ A comparison of the rev-vdW-DF2 with other schemes, including PBE, PBE-D2,²³⁾ and optB86b-vdW,^{24,25)} are shown in Fig. S3 in the online supplementary data at http://stacks.iop.org/JJAP/57/055703/mmedia.

Ion cores were replaced with Troullier–Martins normconserving pseudopotentials for the Si atoms and ultrasoft pseudopotentials for the C, H, O, F, and Pt atoms.²⁶⁾ Valence wave functions and charge densities were expanded in the plane wave basis sets with cut-off energies of 36 and 400 Ry, respectively. A $3 \times 2 \times 1$ uniform *k*-point mesh was used

Fig. 2. (Color online) Atomic geometries at (a) IS, (b) MS, (c) FS, and (d) energy profile of the reaction pathway with water. across the entire surface Brillouin zone. The reaction pathways were calculated by using a climbing image nudged elastic band method (CI-NEB).^{27,28)} For each CI-NEB calcu-

(b) MS

(c) FS

across the entire surface Brillouin zone. The reaction pathways were calculated by using a climbing image nudged elastic band method (CI-NEB).^{27,28)} For each CI-NEB calculation, eight intermediate images between every two stable states have interpolated the geometries of the progressed reaction. Optimization was performed iteratively until the residual forces acting on all of the atoms at the saddle point and in-plane forces of the remaining images were reduced to below $10^{-3} E_{\rm h}/a_0$ and $2 \times 10^{-3} E_{\rm h}/a_0$, respectively, where $E_{\rm h} = 27.211 \,\text{eV}$ and $a_0 = 0.529 \,\text{Å}$. In order to simplify the models, all of the calculations were performed at zero temperature and without considering the effects of the water solvent.

3. Results and discussion

3.1 Reaction pathway

(a) IS

In the absence of a catalyst, the reaction pathway with the lowest activation barrier was found to be similar to that of non-catalytic SiC etching with HF.¹⁴⁾ In the first step, from the initial state (IS) to the metastable state (MS), a water molecule transfers a proton to the terminating OH group of the targeted Si atom, resulting in the adsorption of a water molecule on the step-edge Si. Meanwhile, OH⁻ is adsorbed on the step-edge Si, forming a five-fold coordinated MS and resulting in the elongation of the Si–C backbond. In the following step from the MS to the final state (FS), a proton from the adsorbed water molecule is transferred to the C of the Si–C back bond and results in its dissociation.

The atomic configurations of the IS, MS, and FS are shown in Figs. 2(a), 2(b), and 2(c), respectively. The energy profile of this reaction is shown in Fig. 2(d). The activation barrier of this reaction pathway is 1.93 eV. This relatively large activation barrier is consistent with the experimental results, indicating that the SiC surface cannot be etched by water in the absence of a catalyst.

The interaction of water solvent with Pt surfaces is quite different as compared to that of HF. HF adsorbs weakly and molecularly on Pt without dissociation.²⁹⁾ However, water molecules adsorb onto stepped Pt surfaces with adsorption energies of ca. 0.5 eV and tend to dissociate into OH and H which co-adsorb onto a step-edge of the Pt surface.^{30,31)}

In our previous study of the Pt-catalyzed HF etching of SiC,¹⁴⁾ we found that the activation barrier mainly depends on the separation of SiC and Pt along the *z*-direction. Given



Fig. 3. (Color online) Atomic geometries of the *z*0 model at (a) IS, (b) MS1, (c) MS2, and (d) FS.

that we employ the same distance of Pt and SiC surfaces as that in the previous study. This model of etching using water $(z = 0 a_0)$ is also defined as z0 model (Fig. 3), in which the distance of the targeted Si and the topmost Pt layer is ca. 14.6 a_0 along the z-direction.

The reaction pathway of the Pt-catalyzed SiC etching with water involves three steps. The first step (IS to MS1) involves the dissociative adsorption of water onto a step-edge of the Pt surface. In the second step (MS1 to MS2), the OH⁻ adsorbed on the Pt surface moves towards the target Si atom, forming a Pt-O-Si chain and a five-fold coordinated Si at MS2. In the third step (MS2 to FS), the proton of the terminal OH group of the Si atom is transferred to the C of the Si-C back-bond, resulting in its cleavage at the FS. The side view of the atomic geometries of z0 model at the IS, MS1, MS2, and FS are shown in Figs. 3(a), 3(b), 3(c), and 3(d), respectively. In the z0 model, the shortest distances between Pt and the terminal O in the MS2 and FS were calculated to be 2.1 and 2.14 Å, respectively. The activation barrier is calculated as the energy difference between the MS1 and the transition state from MS2 to FS. The activation barriers of the z0 model and the one where Pt is located at $z = 0.5 a_0$ (named z0.5 model) higher compared to the z0 model are 0.61 and 0.79 eV, respectively (Fig. 4). These activation barriers allow etching at room temperature.

3.2 Mechanochemical interaction

The calculated activation barriers were found to depend significantly on the position of the Pt catalyst along the *z*-direction. Figure 5 shows the relative energies of the IS, MS1, MS2, and FS as a function of the Pt–SiC separation along the *z*-direction. The IS, MS1, MS2, and FS energies are stabilized as Pt moves toward the SiC surface and exhibit minimum values at $z = 0.5 a_0$ because of the formation of



Fig. 4. (Color online) Energy profiles for the reaction pathways of the z0 and z0.5 models.



Fig. 5. (Color online) Relative energies of the IS, MS1, MS2, and FS as a function of the Pt–SiC separation along the *z*-direction.



Fig. 6. (Color online) Total force exerted on the Pt along the *z*-direction at IS, MS1, MS2, and FS.

Pt–O bonds (Fig. S4 in the online supplementary data at http://stacks.iop.org/JJAP/57/055703/mmedia), which lowers the total energy of the system.

By changing Pt position along the z-direction, the total forces exerted on the Pt layer along the z-direction were calculated and shown in Fig. 6. The total forces increase monotonically as Pt moves toward the SiC surface and become close to zero at around z0.5 model. This procedure can mimic the applied pressure parameter used in the experiments. However, the comparison between the calculated forces and those measured under the experimental etching

conditions is difficult because the contact area between the Pt and SiC surfaces in the experimental etching process is unknown due to the roughness of both surfaces. Thus, forces exerted on some parts of the contact area are larger than others. Furthermore, in the experiment, the force exerted on Pt surfaces is a mean value over the whole surface. Therefore, due to the inaccurate estimation of forces exerted on the Pt layers under the experimental conditions, the estimation is based on the mean value of the force between the probing tip and the sample in an atomic force microscope. The average of the total forces exerted on the Pt layer in the z0 model is 1.5 nN, which is comparable to the mean value of the force between the probing tip and the sample in an atomic force microscope operating in the non-contact mode.^{32,33}) Therefore, the forces exerted on Pt and SiC in the z0 model are insufficient to damage the surfaces. Moreover, the activation barrier in this model is relatively low, implying that $z = 0 a_0$ is an appropriate position for etching at room temperature.

The physicochemical interactions at the Pt-SiC interface can be divided into elastic and chemical interactions, which are characterized by the total forces exerted on Pt along the z-direction and the total energy of the system. The elastic interactions originate from the deformation or distortion of atoms at the SiC-Pt interface and destabilize the system, as seen from z = 0.5 to $-0.5 a_0$. In contrast, the chemical interactions relate to bond formations between the two surfaces and stabilize the system, as seen from z = 2.5 to $0.5 a_0$ (Figs. 5 and 6). This stabilization is the most pronounced in the five-fold coordinated states (MS2) of the models with Pt catalyst (Fig. 4) compared to that of the non-Pt model (denoted by MS) [Fig. 2(d)]. The energy difference between the MS and the IS in the no-Pt model is +1.44 eV, whereas that between the MS2 and the IS in the z0.5 model is $-0.15 \,\mathrm{eV}$. The corresponding activation barriers of the two models reduce from 1.93 eV (no-Pt model) to 0.79 eV (z0.5 model). Additionally, further lowering of the activation barrier in z0 model is due to the destabilization of the IS, MS1, and FS states relative to the MS2 state. The destabilization of the former three states can be attributed to elastic interactions and are consistent with the previous study that showed the MRR dependence on rotational speed and pressure.¹⁶⁾ However, in total, the chemical interactions related to bond formations between the two surfaces are dominant and stabilize the system (Fig. S5 in the online supplementary data at http://stacks.iop.org/JJAP/57/055703/mmedia). Therefore, we concluded that the lower activation barrier in the presence of the Pt catalyst is mainly due to the chemical stabilization resulting from the formation of Pt-O bonds at the Pt-SiC interface. Accordingly, the reaction will be promoted by tuning the binding energy with O using other catalysts.

3.3 Activation barrier of the etching in water and HF We have re-calculated the activation barrier for the first Si–C bond breaking in HF using the same reported model and pathway.¹⁴⁾ By employing the long-range dispersion correction, the activation barrier of the *z*0 model is increased from 0.78 to 0.80 eV due to the stabilization of the IS energy compared to that of the FS (Fig. S6 in the online supplementary data at http://stacks.iop.org/JJAP/57/055703/mmedia). The dependence of the total energies and total forces exerted on the Pt layer at IS, MS, and FS are re-calculated (Fig. S7 in the online supplementary data at http://stacks.iop.org/JJAP/57/

055703/mmedia). The total energies exhibit minimum at *z*0 model, which is similar to the previous calculation.

Activation barriers for the etching in water and that in HF are quite similar. The activation barrier of the first Si–C bond breaking with HF is slightly higher than that with water due to the difference of the Pt position in the x- and y-directions. Therefore, it is not appropriate to compare the activation barrier of the two cases. Based on our current simplified modeling and assumption, however, the calculated activation barriers qualitatively show a possibility for the chemical reactions to take place at the Pt–SiC interfaces.

4. Conclusions

While it may be necessary to study the entire catalytic cycle of the removal of Si from the surface of SiC in order to completely understand the removal mechanism, our study describes a plausible mechanistic pathway for the Ptcatalyzed etching of SiC in water. The proposed mechanism is similar to that of Pt-catalyzed etching with HF. A water molecule dissociates and adsorbs on a step-edge Si atom, forming a five-fold coordinated Si moiety in the MS2. The SiC-Pt system is stabilized by the formation of Pt-O-Si chains, which lowers the activation barrier for the etching of SiC in water. The obtained data indicate that the activation barriers are strongly dependent on the physicochemical interactions of the two surfaces. However, chemical interactions between the surfaces are the dominant factor and primary contributors to the promotion of the reaction. By tuning the binding energy with O using other catalysts, the chemical interactions and the etching will be promoted. Using Pt as a catalyst, the activation barriers for the etching with water and HF are low enough for the etching to proceed at room temperature. As a result, in CARE with HF, co-etching by HF and water takes place, leading to both OH- and F⁻ terminations.

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