

## High-efficiency SiC polishing using a thin film catalyst in pure water

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### Abstract

A novel abrasive-free method called catalyst-referred etching (CARE) is used for planarization of SiC. In this method, a thin platinum (Pt) catalyst layer is deposited on an elastic pad. The planarization is performed by rotating the catalyst pad in contact with a wafer surface in water. After the planarization, SiC surfaces are atomically smooth with a root-mean-square (RMS) roughness of less than 0.1 nm over a whole wafer. Thanks to the use of pure water as the etchant, CARE is an environmentally friendly planarization method and potentially applicable to planarization of many functional materials, including GaN and oxides surfaces. However, the practical application of CARE is limited due to its low material removal rate (MRR) when using a Pt catalyst. Therefore, improving its MRR is highly demanded. Our recent research indicated that the etching proceeds via dissociative adsorption of water molecules onto Si–C bonds at topmost Si atoms. 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. Therefore, we experimentally investigate the dependence of MRR on various catalyst materials. The study reveals that Ni and Ru have high catalytic performance. Compared to Pt, Ni and Ru have the higher binding energy with O. The stronger chemical bonds promote water dissociation and stabilization of chemical bonds at the catalyst–SiC interface, leading to lowering its activation barrier and enhancement of the etching reaction.

Catalyst-referred etching, Planarization, Catalyst, Wide bandgap semiconductors

### 1. Introduction

Planarization method plays an important role in the production of electronic and optical devices because any uncompleted removal or irregularities on the surface such as scratches can cause the non-uniform thickness of the oxide layer, killer defects, unwanted scattering, and lower reflectivity. To fulfil the growing demands and requirements of high accuracy processing, chemical mechanical planarization (CMP) is chosen as a finishing planarization method because it offers significant advantages in excellent global planarization and applicable to wide-range of materials from dielectric to metal oxides such as GaN [1-3], SiC [4], and sapphire [5]. However, there are many limitations still remained such as scratches and mechanical defects induced from anomalously large particles in the slurry [6], and corrosive attacks caused by the residual particles on the polished surface [7].

To overcome such limitations, chemical planarization using a catalyst pad in aqueous solutions called catalyst-referred etching (CARE) has been proposed [8-10]. In this method, the removal only takes place chemically at contact areas of the wafer and the catalyst pad. During the rotation, the pad is alternatively contacted the higher points of the wafer surface to etch. Therefore, based on this concept, a geometrically and highly ordered surface can be produced. Using Pt as a catalyst, the material removal rate (MRR) of CARE for SiC has been reported to be ca. 20 nm/h [11]. The low MRR using a Pt catalyst limits the CARE performance in the practical application. Therefore, improving the MRR is highly demanded.

Our recent research indicates that the etching proceeds via dissociative adsorption of water molecules onto the Si–C bonds

at the topmost Si surface, as shown in Fig. 1. The lower activation barrier is mainly due to the chemical stabilization of the five-fold coordinated Si state at metastable state 2, resulting from the formation of Pt–O bonds at the Pt–SiC interface [12]. We expect that the CARE performance can be improved by tuning the binding energy of the catalyst with O. The present work, therefore, is undertaken to find the best catalyst for CARE by investigating the dependence of the MRR on catalysts.

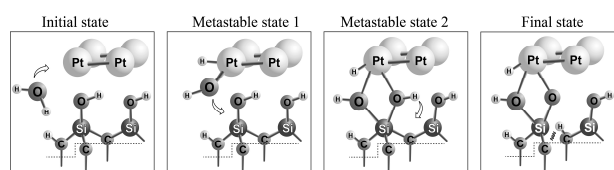


Figure 1. Mechanistic reaction pathway of SiC in water using a Pt catalyst.

### 2. Experimental setup and conditions

The schematic diagram of CARE is shown in Fig. 2.

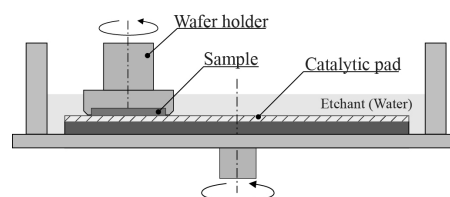


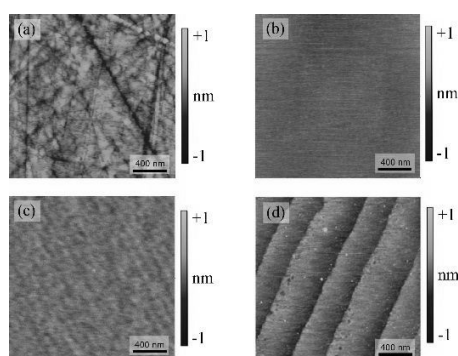
Figure 2. Schematic diagram of the chemical planarization method using Pt catalyst in water

Catalyst with a thickness of ca. 50 nm was deposited on a rubber pad, which has grooves on its surface to supply water for the etching. To keep the wafer and the pad contacting, a pressure of 40 kPa was applied on the backside of the wafer. The catalyst pad and wafer were immersed in water and were independently rotated on its axis along the same direction in the two parallel planes. The rotational speeds of the chamber and the wafer holder were 10.0 and 10.1 rpm, respectively.

In this study, we used commercially available 2-inch 4H-SiC (0001) substrate to check the dependence of MRR on various catalysts. After the planarization, the surfaces were rinsed with water. The MRR was calculated from the weight difference of the before and after planarization. The planarized surface was observed by atomic force microscopy (AFM, Digital Instruments, Dimension 3100).

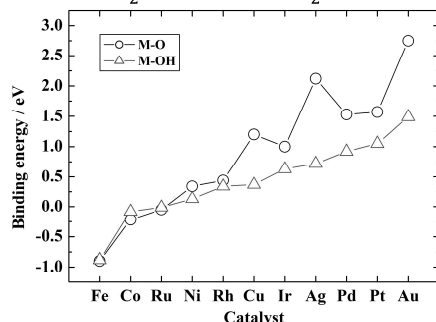
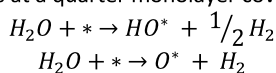
### 3. Experimental results

Figure 3 shows AFM images of (a), (b) 4° off-axis cuts and (c), (d) on-axis cuts of 4H-SiC surfaces, where (a) and (c) are as-received surfaces and (b) and (d) are SiC surfaces planarized via CARE in water. As shown in Fig. 3 (d), smooth SiC surfaces consisting of atomically flat terraces with a single bilayer step height were produced via CARE in water. The MRR of CARE for the on-axis and the 4° off-axis wafers were 1–2 nm/h and 19 nm/h, respectively [11].



**Figure 3.** AFM images ( $2\ \mu\text{m} \times 2\ \mu\text{m}$ ) of (a, b) 4° off-axis cuts and (c, d) on-axis cuts of 4H-SiC surfaces, in which (a, c) are as-received and (b, d) are planarized via CARE in water. The corresponding RMS values are (a) 0.67 nm, (b) 0.06 nm, (c) 0.17 nm, and (d) 0.08 nm [10].

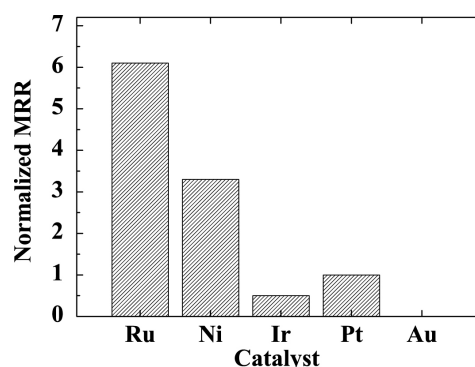
As seen in Fig. 1, the etching reaction is promoted by the chemical stabilization at the five-fold coordinated state via forming Pt–O bonds at the interface. Therefore, we expected that the MRR can be improved by tuning the binding energy of the catalyst with O. Nørskov et al. calculated reaction heats for the below reactions over the most close-packed surface of a number of metals at a quarter monolayer coverage [13],



**Figure 4.** The dependence of binding energy with O and OH on catalyst metals.

where  $H_2O$  and  $H_2$  are in the gas phase and \* denotes a site on the surface. The positive value means that the final states are less stable, i.e. the binding energy with O and OH are weak and vice versa. The results are summarized in Fig. 4.

We select some catalysts including Ru, Ni, Ir, and Au and experimentally test their performance. The dependence of MRR on catalyst metals is shown in Fig. 5. In this plot, the MRR using a Pt catalyst is taken as unity. Au shows no catalytic reactivity in CARE because of its low binding energy, while Ir has a moderate reactivity. Among the investigated catalyst, Ni and Ru have the highest MRRs which are ca. 3 and 6 times higher than that of a Pt. This trend of MRR is correlated to the binding energy trends plotted in Fig. 4. However, the MRR using Ru or Ni catalyst is time decayed, meaning that the MRR is reduced with the processing time. Compare to Pt, Ru and Ni are quite active elements. Under the experimental conditions, their surface might be oxidized or poisoned by adsorbates in the etching solution. This might be a possible reason for the MRR decay observed in Ru and Ni.



**Figure 5.** The dependence of MRR on catalyst metals.

### 5. Conclusion

CARE with water and a catalyst can be used to planarize 4H-SiC to atomically smoothen surfaces. CARE performance is improved when Ru or Ni is used as a catalyst. The MRR using Ni and Ru were found to be ca. 3 and 6 times higher than that using a Pt catalyst. However, the MRR using Ru and Ni catalysts are time decayed due to strong chemical bonds with O and OH, leading to poisoning or hindering the chemical reaction. It is important to modify the M–O and M–OH binding energies (M=Ru or Ni) for the long-term catalyst usage. The advantages of CARE and the understanding of the CARE mechanism are crucial for its practical application in industry as an environmentally friendly and sustainable planarization method.

### Acknowledgments

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