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

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**Abstract**
A novel abrasive-free method called catalyst-referred etching (CARE) has been developed in our group. In this method, a platinum film as a catalyst is deposited on an elastic pad that is rotated in contact with a wafer surface in water. After CARE planarization, SiC surfaces are atomically smooth with a root-mean-square (RMS) roughness of less than 0.1 nm over a whole wafer. Using only pure water as an etchant, CARE is a promising planarization method and potentially applicable to planarization of many semiconductor surfaces, including GaN and oxides surfaces. However, the removal rate (RR) of SiC via CARE using a Pt catalyst is quite low, limiting its practical application. Our recent research on the removal mechanism using density functional theory (DFT) calculations indicated that the etching proceeded via a dissociative adsorption of water molecules onto the Si–C bonds at the topmost Si surface, catalyzed by a Pt catalyst. We expect that the RR can be improved by using the higher reactivity catalyst. Therefore, we experimentally investigate the dependence of RR on various catalyst materials. The results indicate that SiC can be planarized with a high RR using 3*d* transition metal catalysts. Using DFT calculations, we clarify that a high catalytic reactivity of a 3*d* transition metal is attributed to the higher chemical binding energy with OH, compared to that of Pt. This high chemical bond promotes water dissociation and stabilizes metastable states by forming chemical bonds at the catalyst-SiC interface, leading to lowering its activation barrier and an enhancement of the etching reaction.

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

## 1. Introduction

SiC exhibits excellent physical and chemical properties and is close to becoming a material for high-power, high-temperature, and high-voltage applications. In such applications, well-prepared surfaces are of crucial importance to achieve their theoretical performances. However, SiC is a hard and inert material, making the production of a smooth surface via conventional polishing methods difficult. In this context, a new abrasive-free planarization method called catalyst-referred etching (CARE) has been proposed and developed in our group [1-5]. In this method, a catalytic functionality is added to a pad surface; then, etching is preferentially induced at the topmost parts of the workpiece surface, which are most frequently in contact with the catalyst, as shown in Fig. 1. As a result, smoothening efficiently proceeds like mechanical polishing but chemically.

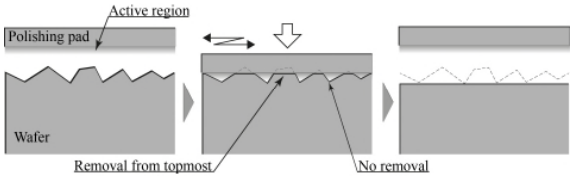


**Figure 1.** Conceptual diagram of catalyst-referred etching (CARE) method.

## 2. Experimental setup and conditions

All experiments are carried out using CARE apparatus [6]. Catalyst was deposited on a rubber pad, which has grooves on its surface to support the diffusion of water as an etchant onto the wafer surface. The thickness of the Pt layer on a rubber pad was approximately 100 nm. Wafer was introduced to a wafer holder that equipped with a pressure controller. A pressure of 400 hPa was applied on the backside of the wafer to keep the wafer and the pad contacting. In the processing, the catalyst pad and wafer were immersed in deionized (DI) 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.

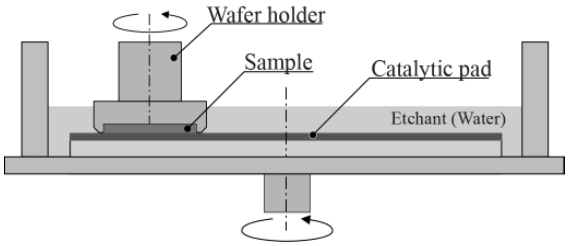


**Figure 2.** Schematic diagram of CARE using Pt catalyst in water

In this study, we used commercially available 2-inch 4H-SiC (0001) substrates for CARE processing. The removal rate was calculated from the weight loss after the planarization. The planarized surface was observed by an 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 obtained structure indicates that the removal proceeds from a step-edge to a terrace site, a step-flow etching type. The removal rates (RR) of the on-axis and the 4°-off-axis wafers were 1–2 nm/h and ca. 20 nm/h, respectively [6].

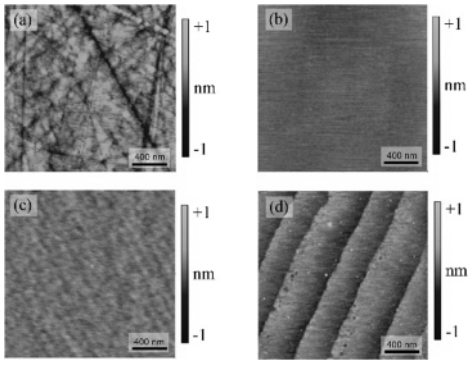


**Figure 3.** AFM images (2 μm × 2 μm) of (a, b) 4° off-axis cuts and (c, d) on-axis cuts of 4H–SiC surfaces, in which (a, c) are as-received and (b, d) are planarized via CARE in water. The corresponding RMS values are (a) 0.668 nm, (b) 0.064 nm, (c) 0.169 nm, and (d) 0.075 nm.

## 4. Catalyst role of Pt

Our recent research on the removal mechanism using density functional theory (DFT) calculations indicated that the etching is proceeded via a dissociative adsorption of water molecules onto the Si–C bonds at the topmost Si surface, catalyzed by a Pt catalyst (Fig. 4) [7]. The first step from the initial state (IS) to metastable state 1 (MS1) involves the dissociative adsorption of water on a step-edge of the Pt surface. In MS1, both $H^+$ and $OH^-$ from the water molecule are adsorbed on a step-edge of the Pt surface. In the second step, from MS1 to metastable state 2 (MS2), the $OH^-$ terminating a step-edge Pt adsorbs on the targeted Si atom, forming a Pt–O–Si chain. Consequently, a five-fold coordinated Si is formed in MS2. In the third step (MS2 to final state (FS)), the proton of the terminal OH group of the targeted Si atom is transferred to the C of the Si–C back-bond, leading to its cleavage. The barrier height of the Si–C back bond breaking with the Pt catalyst is calculated to be 0.79 eV, which is small enough to proceed at the room temperature.

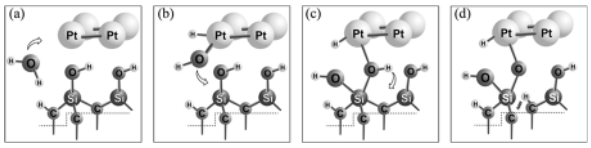


**Figure 4.** Reaction pathway of the Pt-catalyzed water etching of a SiC surface: (a) initial state, (b) dissociative adsorption of water onto the Pt surface, (c) five-fold coordinated Si state stabilized by a chemical Pt–O bond, and (d) Si–C bond cleaved in the final state.

## 5. Performance of 3*d* transition metal catalysts

Using only pure water as an etchant, CARE is a promising planarization method and potentially applicable to planarization of many semiconductor surfaces, including GaN and oxides surfaces. However, the RR of SiC via CARE using a Pt catalyst is quite slow, limiting its practical application. Moreover, CARE using water as an etchant, various catalyst metals become candidates. Based on our understanding of the catalyst role and removal mechanism, the RR can be improved by using a catalyst with the higher catalytic reactivity. Due to the cost-effectivity of 3*d* transition metals, we experimentally examine the dependence of RR on these catalysts.

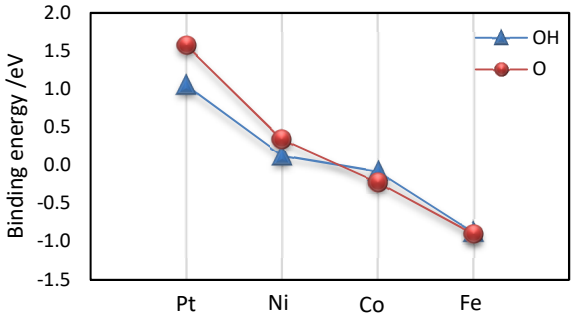


**Figure 5.** Binding energies of O and OH on Pt, Ni, Co and Fe.

Among the investigated catalysts, we found that the RR using a Ni catalyst is the highest, which is several times higher that that using a Pt catalyst. The higher RR using a Ni catalyst can be explained by the higher binding energy of O/OH with Ni compared to that of a Pt [8]. This higher binding energy will improve the stabilization of the five-fold coordinated Si state at MS2 (Fig. 4 (c)). The RR using a Fe catalyst is not so high. This is considered due to the too strong binding energies of O and OH with the Fe. The results indicate that the optimization of the binding energy of O/OH on a catalyst surface is of importance.

## 6. Summary

CARE with pure water and a thin film catalyst can be used to planarize 4H-SiC to atomically smoothen surfaces. Ni is a promising catalyst candidate for a high-efficiency planarization of SiC via CARE. The advantages of CARE and the detail understanding of the mechanism are crucial for its practical application in industry as an environmentally friendly and sustainable technology for the planarization of semiconductor devices.

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