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# Development of high efficiency polishing method using pure water and Ni catalyst

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#### Abstract

We have developed "Catalyst Referred Etching" (CARE) using pure water as an etchant and Pt as a catalyst as a new polishing method. Using CARE, many functional materials, such as silicon carbide (SiC), gallium nitride (GaN), and metal oxides, can be planarized to atomically well-ordered surfaces with a root-mean-square (RMS) roughness of less than 0.1 nm over a whole wafer. The planarized surface has a step-and-terrace structure, indicating that CARE is step-flow etching type. Thus, the material removal rate (MRR) of CARE using a Pt catalyst, especially for crystalline materials, is quite low, approximately 20 nm/h for SiC. Our recent study shows that the catalytic reactivity of a Ni for CARE is higher than that of a Pt. Additionally, compared to Pt, Ni is cost-effective and abundant, indicating that Ni is a promising catalyst for CARE. However, the MRR using a Ni catalyst usually decreases with the processing time due to catalytic deactivation by oxidation of the Ni surface. Therefore, we use electrochemical deposition method to control Ni surface condition and to keep its surface catalytivally active. First, before CARE processing, the Ni is deposited on a polishing pad by setting its potential to be lower than that of the etchant. The deposited Ni layer works as an active catalyst. Second, after CARE processing, the residual Ni is dissolved into the etchant by changing its potential to be higher than that of the etchant. By alternative repeating these steps, reactive Ni on the polishing pad is continually prepared. Accordingly, the removal rate is stable with processing time. The study reveals that CARE with the potential control method is potential for high-efficiency polishing of functional materials. The keywords : functional material, polishing, step-flow type etching, catalyst, transition metal, nickel, potential control

## 1. Introduction

Silicon carbide (SiC) is a promising material used as a substrate for the next generation electronic devices because it has excellent physical properties, such as wide band-gap, high breakdown voltage, high saturated electron velocity and high thermal conductivity. Thanks to these properties, SiC is suitable for devices that operate in high temperature and high voltage. However, commercially available SiC devices usually have lower performance than their theoretical expectation due to problems such as the non-uniform thickness of the oxide layer and killer defects. In order to achieve their ideal performances, atomically well-ordered surfaces must be prepared. However, SiC is an extremely hard and chemical inert material, making preparation of a smooth SiC surface difficult. Therefore, we developed a new polishing method called "Catalyst Referred Etching (CARE)" [1-4]. Fig. 1 shows a conceptual diagram of the planarization method .



Figure 1. CARE conceptual diagram

action proceeds via chemical etching, assisted by a catalyst. Previously, using Pt as a catalyst, we successfully applied CARE in pure-water to planarize SiC, GaN and metal oxides surfaces. The water-CARE processed surface is atomically smooth with one-bilayer height step-terrace structure. The obtained surface structure indicated that CARE is step-flow etching. Consequently, the material removal rate (MRR) is very slow and is approximately 20 nm/h for SiC [5], limiting the practical application of CARE. Our recent study shows that the MRR depends on trasition metal catalyt, as shown in Fig. 2, and the MRR using a Ni is 13 times higher than that using a Pt. Moreover, Ni is more cost-effective than Pt. Therefore, Ni is a promising catalyst for CARE. However, the MRR usually decreases with processing time because the Ni surface is oxidized easily in pure water, and the catalytic activity decreases. Therefore, it is diffcult to use a Ni catalyst for a long processing time. In this paper, we propose a stable utilization method to keep the Ni surface active.

with the polishing pad are selectively removed. The removal re-



In CARE, a polishing pad with a catalytic function works as a reference plane. Only the top most sites of a sample contacted

Figure 2. The dependence of the MRR on transition metal catalysts; the bars show the removal rate and the black triangles show the dorbital occupancy

## 2. Concept of a stable utilization method of Ni catalyst

We propose the electrochemical method to control Ni surface condition and to keep the Ni surface catalytical active. Fig. 3 shows the conceptual scheme of controlling Ni surface condition. In this method, an acid chemical solution many Ni ions is used as an etchant and a polishing pad is used as an electrode. First, before CARE processing, the Ni is deposited on the polishing pad by setting its potential to be lower than that of the etchant. The deposited Ni layer works as an active catalyst. Second, after CARE processing, the residual Ni is dissolved into the etchant by changing its potential to be higher than that of the etchant. By alternative repeating these steps, reactive Ni on the polishing pad is continually prepared.



**Figure 3.** Conceptual scheme of controlling Ni surface condition; V<sub>et</sub> and V<sub>pol</sub> are the potential of the etchant and the polishing pad. (a) V<sub>pol</sub> becomes lower than V<sub>et</sub>, and Ni is deposited. (b) V<sub>pol</sub> becomes higher than V<sub>et</sub>, and Ni is dissolved

#### 3. Results and discussion

We used 4H-SiC (0001) 4° off-axis as a sample. Table 1 shows the experimental condition. In this study, Au was used as an electrode because Au is chemical stable, and doesn't work as a catalyst as shown in Fig. 2. We used standerd hydrogen electrode (SHE) as a reference electrode. For the electrochemical deposition, we used H<sub>2</sub>SO<sub>4</sub> pH3 and NiSO<sub>4</sub> 0.01 M solution as the etchant. In this experiment, H<sub>2</sub>SO<sub>4</sub> is used to promote the dissolution of residual Ni; however, H<sub>2</sub>SO<sub>4</sub> may be unnecessary once the applying voltage pattern is optimized in the future. In this experiment, three phases were repeated continuously, as shown in the Fig. 3. To deposite Ni on the polishing pad, a voltage of -0.5 V vs. SHE was applied onto its surface. After the deposition, the experiment was carried out under open circuit potential. Finally, the residual Ni was removed by applying a voltage of 1.0 V vs. SHE. Total time for a cycle was 550 s. Total processing time was 480 min. The removal rate was calculated from the weight loss that occurred during processing, which was measured using an electronic balance. The MRR was measured every 90 min and shown in Fig. 5. The MRR was stable using this method. The result indicates that this potential control method can keep catalytic performance of Ni high and realize high efficiency polishing technique.

## 4. Summary

In CARE, the MRR depends on the transition metal catalysts. The MRR using a Ni catalyst is 13 times higher than that of using a Pt. However, the MRR using a Ni catalyst decreased with the processing time because the Ni surface was easily oxidized. Therefore, we suggested an electrochemical deposition method to keep Ni surface active. In NiSO<sub>4</sub>, repeating Ni deposition and dissolution realized stable processing rate of SiC for at least 6 hs. The result indicates that variety of transition metals can work as catalysts in CARE by using this method and in addition, the high efficiency polising technique is found. **Table 1** Experimental condition

Sample	2 inch 4H-SiC(0001) 4°off
Etchant	H <sub>2</sub> SO <sub>4</sub> : pH3
	NiSO4 : 0.01 M
Electrode	Au
Processing time	120 min× 3 times
Processing pressure	300 hPa
Relative speed	24 cm/s



**Figure 4.** Illustration of applied voltage pattern; In phase A, -0.5 V was applied to deposit Ni. In phase B, the experiment was carried out under open circuit potential to process SiC. In pahse C, 1.0 V was applied to dissolve Ni.



**Figure 5.** Time dependence of the MRR; the black filed circles are the result using this method and the black filed triangles are the result using sputtered Ni

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