

Investigation of catalytic metals for a catalyst referred etching in pure water

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Abstract

The preparation of atomically smooth surface on many kinds of functional materials used in semiconductor or optical devices is still a fundamental and technological issue. For example, some difficult-to-machine materials, such as SiC, GaN, and Sapphire, have been attract attentions to be flattened atomically in these applications. We have proposed a novel planarization method, named catalyst-referred etching (CARE), which can flatten a surface by chemical etching in pure water with assistance of catalysis of Pt. The etching mechanism in the CARE has been understood to be a dissociative adsorption of H₂O molecule, so-called hydrolysis reaction, to the back-bond of a top-most atom. SiC, GaN, and some oxide materials can be flattened atomically by the CARE. However, the usage of Pt costs a lot, and its contamination, which causes serious damage for semiconductor devices, is difficult to be removed. In this study, transition metals, which can assist the dissociative adsorption of molecules, were studied as a catalyst alternative to Pt. Nickel (Ni [3d⁸, 4s²]), copper (Cu [3d¹⁰, 4s¹]) and gold (Au [4d¹⁰, 5s¹]), which have different number of d-electrons, were investigated. Material removal rate (MRR) of SiO₂ and SiC samples were evaluated. The MRRs of SiO₂ and SiC by using Ni were about 4 times and 13 times higher than that by using Pt, respectively. In the case of Cu and Au, the MRRs of both samples were almost 0 nm/h. This result indicates Ni has highest catalytic activity in the CARE. A general knowledge that d-character determines the catalytic activity of transition metals for the dissociative reaction also applicable to understand the CARE process.

catalyst; etching; silicon carbide; silicon dioxide; pure water

1. Introduction

Preparation method of an atomically smooth and crystallographically ordered surface is highly demanded in many functional materials used in devices of semiconductor or precision optics. For examples, surface preparation methods for SiC, GaN, sapphire and SiO₂ are still needed to be improved. To meet such requirement, we have developed a novel chemical planarization technique, in which we employ an etching reaction proceeding with an assistance of catalyst [1]. The name of this method is catalyst referred etching (CARE). In the beginning, Pt was used as a catalyst despite its higher cost and its contamination on a wafer, which causes severe problem in semiconductor applications because highly corrosive HF was used as etchant. In recent years, we have found that CARE using pure water as etchant (named the Water-CARE) can flatten many materials, such as SiC, Al₂O₃, and α -quartz [2,3]. By running the first-principles calculation, the etching mechanism, in theory, is proposed to be an indirect dissociative adsorption of a water molecule to the back bond, so-called indirect hydrolysis reaction [4]. In this study, Water-CARE using other transition metals, which are known to assist the dissociative adsorption of molecules, as a catalyst alternative to Pt was applied to SiC and SiO₂ surfaces to evaluate their catalytic activity.

2. Experimental setup

Ni [3d⁸, 4s²], Cu [3d¹⁰, 4s¹], and Au [4d¹⁰, 5s¹], which have different number of d-electrons, were investigated because the occupancy of the d-band affects the characteristics of chemisorption on metal surface [5–7]. Experimental conditions are shown in Table 1. 4H-SiC (0001) 8° off-axis and SiO₂

(amorphous glass) substrates were used as samples. In this study, a local CARE system, shown in Fig. 1, was employed. Only the limited area on the sample surface, where contacts with catalyst, is etched off. In this system, catalytic metal film was deposited on an O-ring made of a rubber. Sample surface are rubbed by the catalyst deposited O-ring. Figure 2 shows a typical etching mark measured by a scanning white light interferometry (ZYGO, New View). The removal rate was evaluated by the depth of the mark.

Table 1. Experimental conditions.

Sample	4H-SiC (0001)	SiO ₂
	8° off-axis	24 rpm
Time	1 h	5 min
Etchant	Pure water	
Rotational speed	24 rpm	
Pressure	2000 hPa	

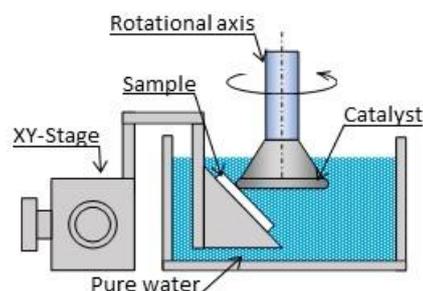


Figure 1. The local area etching system of the CARE.

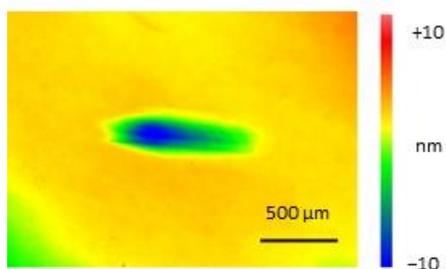


Figure 2. A typical etching mark measured by New View.

3. Results and Discussion

The removal rates of SiC and SiO₂ were shown in Fig. 3 and 4, respectively. They were faster in the order of Ni, Pt, Cu, and Au. The removal rates of SiO₂ and SiC by using Ni were about 4 times and 13 times higher than those by using Pt, respectively. In the case of Cu and Au, the removal rates were extremely slow. In particular, they were almost 0 nm/h in the case of Au. The percentage of the filling of the d-band of each metal is also plotted in Fig. 3 and 4. The removal rates increase as percentage of the occupancy of the d-orbital diminishes. In the removal reaction of the Water-CARE, the first step is understood to be a dissociative adsorption of a water molecule on the Pt surface leading the step-edge Si to be a five-fold coordination situation [4]. The characteristics of the chemisorption on metals are shown in Table 2. In general, for the case of Ni or Pt, the catalytic activity of the chemisorption is known to be higher because they have d-halls, which can easily accept an electron from an adsorbate to bond with it [8]. In contrast, the d-bands of Cu and Au are filled and hardly assist the chemisorption on their surface. This means that the etching reaction in the CARE cannot start. But, in the case of Cu, etching reaction occurs slowly; the removal rates were about 2 nm/h of SiC and 330 nm/h of SiO₂. In pure water, Cu film surface is stochastically oxidized to CuO_x. Because the interaction of Cu with O atoms forms unoccupied d-states near the Fermi level [9], CuO_x can be considered to weakly assist the dissociative adsorption of water molecules leading a slow the removal in the CARE. Nearly the same tendency was observed in the removal rate of SiC and SiO₂, as shown in Fig.3 and Fig4. Consequently, the removal mechanism is elucidated to be common despite the sample materials.

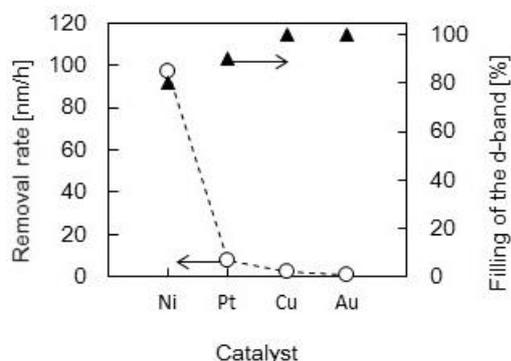


Figure 3. Relation between the removal rate of SiC, the percentage of the filling of the d-band, and catalyst metals.

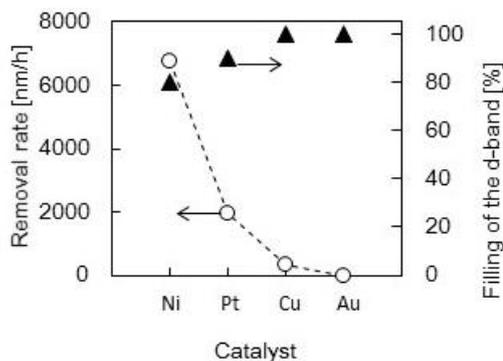


Figure 4. Relation between the removal rate of SiO₂, the percentage of the filling of the d-band, and catalyst metals.

Table 2. The characteristics of chemisorption on transition metals (+: absorbable, -: non-absorbable, ±: weakly absorbable).

Symbol of element	Molecule species				
	O ₂	CO	H ₂	CO ₂	N ₂
Ni	+	+	+	+	-
Pt	+	+	±	-	-
Cu	+	+	-	-	-
Au	-	-	-	-	-

4. Conclusion

Ni, Cu, and Au were studied as new candidates of catalytic metals alternative to Pt in the Water-CARE for SiC and SiO₂. We found Ni has the highest catalytic activity. In contrast, the removal rates were extremely slow in the cases of Cu or Au. In particular, they were almost 0 nm/h in the case of Au. Given this, a general knowledge that d-character determines the catalytic activity of transition metals for the reaction of a dissociative adsorption is also expected to be applicable to understand the Water-CARE mechanism.

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