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Planarization of SiC and oxide surfaces by using Catalyst-Referred Etching with water

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Abstract
A novel abrasive-free planarization method called catalyst-referred etching (CARE) has been invented and developed in our group. In this method, a platinum film, which acts as a catalyst, is deposited on an elastic pad that is rotated in contact with a wafer surface in water. CARE can produce flat, undamaged, and smooth SiC and SiO_2 surfaces with a root-mean-square (RMS) roughness of less than 0.1 nm over a whole wafer. The mechanism is considered a dissociative adsorption of water molecules onto the Si–C bonds at the topmost Si surface. The gross activation barrier strongly correlates with the stability of the metastable state and is reduced by the formation of Pt–O chemical bonds, leading to an enhancement of the etching reaction.

Catalyst-referred etching, Surface reactions, Surface cleaning, Oxide surfaces, Bond formation

1. Introduction

Planarization method plays an important role in production of electronic and optical devices because it can produce high quality surface with low root-mean-square (RMS) roughness and crystally undamaged surface. To fulfil the growing demands and requirements of high accuracy processing and low cost fabrication, many globally polishing methods have been investigated including mechanical polishing, chemical polishing, and chemical mechanical planarization (CMP). Among the proposed planarization methods, 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. These advantages made CMP indispensable for today's microelectronics, semiconductors, and optical components industries in the sense of reliability, stability and cost effectiveness. Many types of substrates have been planarized by CMP such as GaN [1-3], SiC [4], and sapphire [4-5]. However there are many limitations still remained such as scratches and mechanical defects induced from anomalously large particles in the slurry [6], environmental pollution and cleaning room contamination caused by slurry powders [7], or corrosive attacks caused by the residual particles on the polished surface [8].

To overcome such limitations, chemical planarization using a catalyst pad in aqueous solutions called catalyst-referred etching (CARE) has been proposed [9-13]. Unlike conventional planarization method, such as chemical method in which wafer surfaces were isotrophically removed on an entire surface, in this method, the removal only took place at contact areas of wafer and the catalyst pad under the promotion of the chemical reaction by the catalyst pad. In addition, the pad in this method was alternatively contacted the higher points of the wafer surface to etch, which is similar as a pad in CMP. The pad surface was conformed to wafer topography to some extent during the rotation. Therefore, based on this concept, a geometrically and highly ordered surface can be produced.

2. Experimental setup and conditions

The schematic diagram of CARE is shown in Fig. 1.

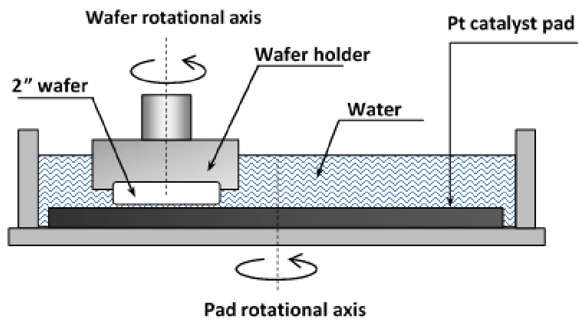

Figure 1. Schematic diagram of the chemical planarization method using Pt catalyst in water

Pt 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. During experiment, the Pt 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.

Table 1. Experimental conditions

Experimental parameters	
Pressure	400 hPa
Etchant	Deionized water
Catalyst	Pt
Wafer	SiO_2 & SiC

In this study, we used commercially available 2-inch silica glass (SiO_2) and 4H-SiC (0001) substrates to investigate the planarization possibility of CARE using Pt catalyst in water. The experimental conditions are shown in Table 1.

After the planarization, the surfaces were rinsed with deionized water. The removal rate 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

The AFM images of as-received and planarized surfaces of silica glass (SiO_2) with an area of 2 µm × 2 µm are shown in Fig. 2 (a) and (b), respectively. A numerous scratches of the as-received surface with the RMS roughness of 0.42 nm is observed. In contrast, after planarization for 1h at the removal rate of about 200 nm/h, the surface were atomically smooth with RMS roughness of 0.15 nm.

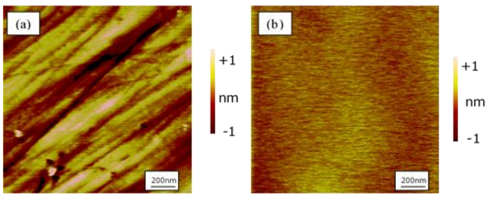

Figure 2. The AFM images (2 µm × 2 µm) of (a) as-received; RMS: 0.42 nm, and (b) planarized surface; RMS: 0.15 nm

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 removal rates of the on-axis and the 4°-off-axis wafers were 1–2 nm/h and 19 nm/h, respectively [14].

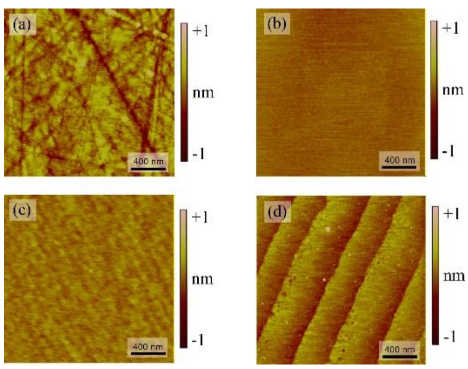

Figure 3. AFM images (2 µm × 2 µm) of (a, b) 4° off-axis cuts and (c, d) on-axis cuts of 4H–SiC surfaces, in which (a, c) are as-received and (b, d) are planarized via CARE in water. The corresponding RMS values are (a) 0.668 nm, (b) 0.064 nm, (c) 0.169 nm, and (d) 0.075 nm.

4. Mechanism of CARE

In contrast to CMP, CARE processing does not require any abrasive particles, which is advantageous for clean room environments. Therefore, understanding the mechanism of CARE is important for its industrial application as a global polishing method. A mechanism of CARE for SiC for breaking the first Si–C bond is proposed and the role of the Pt catalyst in the etching process is investigated based on density functional theory (DFT) calculations.

From first-principles molecular dynamics calculations, using the simulation tool for atom technology (STATE) program package, the reaction pathway is proposed and shown in Fig. 4 [15-16]. 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 Pt as the catalyst is calculated to be 0.71 eV, which is small enough to proceed at the room temperature.

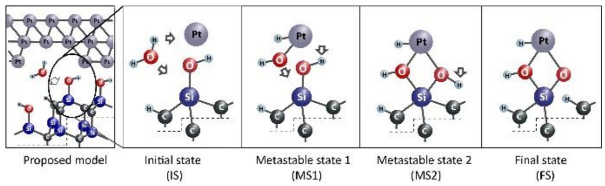

Figure 4. Proposal of reaction pathway of water with SiC and Pt catalyst

The calculated results revealed that the mechanism is the dissociative adsorption of water onto Si–C bonds. This chemical reaction is stabilized by chemical bonding of Pt and O at the SiC–Pt interface, leading to lower reaction barrier for the etching of the SiC. The mechanism of CARE for SiO_2 planarization is also expected to be similar to that for SiC.

5. Conclusion

CARE with pure water and a Pt catalyst can be used to planarize 4H-SiC and SiO_2 to atomically smoothen surfaces. 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 technology for the planarization of semiconductor devices.

Acknowledgements

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