Plasma-based atom-selective etching of sapphire to obtain a damage-free and atomically smooth surface

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Abstract: Herein, we propose a novel smoothing method, namely, plasma-based atom-selective etching (PASE), for sapphire (0001) substrate. The mechanism of PASE is based on the selective removal of surface atoms with more dangling bonds. After PASE, a damage-free and atomically smooth surface with the *S*a roughness of 0.084 nm is obtained, and the material removal rate can be as high as 21.99 μm/min. These results demonstrate the higher efficiency of PASE, compared with chemical mechanical polishing (CMP) based methods.

Keywords: ICP, plasma etching, sapphire, atomic-scale smoothing.

1. Introduction

Sapphire (α-Al_2O_3) is an important ultra-wide bandgap semiconducting oxide crystal with excellent optical, mechanical, and chemical properties [1-4]. For example, it shows superior light transmission, high hardness (9 Mohs), and exceptional chemical inertness [1-4]. Sapphire is now widely used as not only the window material for precision high-energy optics (such as solid laser) but also the substrate material for electronic devices (such as light-emitting diode) [2,3]. Generally, a damage-free and atomic-scale smooth sapphire surface is necessary to fabrication high-performance devices. However, sapphire is a typical difficult-to-machine material due to its prominent hardness and chemical inertness, making it difficult to achieve the ultra-precision smoothing of sapphire [3,4].

Nowadays, chemical mechanical polishing (CMP) is still the most extensively adopted approach for the global planarization of difficult-to-machine materials [3,5,6]. Several modified CMP methods are proposed for the polishing of sapphire. Xu *et al.* compared the sapphire polishing results of traditional CMP and ultrasonic flexural vibration (UFV) assisted CMP (UFV-CMP), and found that UFV-CMP could lead to the smoother surface with the roughness of 0.083 nm and the larger material removal rate (MRR) of 22.8 mg/h [7]. Xie *et al.* developed a novel green CMP slurry with the mixing of silica, sorbitol, aminomethyl propanol, and deionized water. Based on this slurry, they obtained a smooth sapphire surface with the roughness of 0.098 nm and achieved the MRR of 3.268 μm/h [3]. Lei *et al.* proposed La-doped colloidal silica composite abrasive, and the catalytic activity of La could result in the roughness reduction of sapphire from 2.5 nm to 1.2 nm after two-hour CMP [8]. Although these modified CMP methods show the ability to polish sapphire, their efficiency is generally very low as several hours are needed to complete the polishing process. Additionally, due to the heavy loads and hard abrasive particles, sapphire is easily to be damaged or even broken during the processing. Thus, developing highly efficient and damage-free method to achieve the atomic-scale smoothing of sapphire is of vital importance.

In this study, we propose a novel method, namely plasma-based atom-selective etching (PASE), to obtain a damage-free and atomically smooth sapphire (0001) substrate via atmospheric pressure inductively couple plasma (ICP). The polishing mechanism of PASE relies on the selective removal of surface atoms with more dangling bonds at elevated temperature. It is found that after ten-minute plasma etching, an atomical-smooth surface with the *S*a roughness of 0.084 nm can be achieved, and the corresponding MRR can reach as high as 21.99 μm/min. Furthermore, the PASE-treated sapphire shows perfect atomic arrangement without any damage. We strongly believe that our PASE should be a highly-efficient and damage-free approach to fabricate atomic-scale smooth sapphire surface, compared with the CMP-based methods.

2. ICP setup and plasma diagnostics

Fig. 1(a) shows the schematic diagram of ICP setup, which mainly consists of five parts. The three relatively important parts are power supply (matcher, radio frequency (RF) power, inductance coil, and high-voltage (HV) sparker), gas supply (gas cylinder, gas line, and mass flow controller (MFC)), plasma excitation (tube clamp and quartz tube). It should be noted that Ar is used as both cooling and ignition gases, and CF_4 and O_2 are introduced into the Ar-based plasma as reaction gases. The remaining two auxiliary parts are numerical control (NC) machining system (sample holder and 3-axis NC platform) and water-cooling system. Once the power and gas conditions are satisfied, plasma can be generated around the inductance coil. Significantly, to obtain stable plasma torch, the inner and outer quartz tubes should be concentric. Fig.1 (b) shows the image of the real ICP torch, where the plasma presents bright green colour. More details about the setup and processing parameters can be found in Table 1.

Table 1. Setup and processing parameters.

Parameters	Values
Sample	Sapphire (0001) substrate in 10 μm × 10 μm
Frequency of power	27.12 MHz
Power input	500-1000 W
Flow rates of gas	Ignition/cooling Ar gas: 1.5/18.0 slm Reaction CF_4/O_2 gas: 60.0/20.0 sccm
Tube diameter	Inner tube: 14/16 mm inner/outer diameter Outer tube: 18/20 mm inner/outer diameter
Working distance	15 mm
Plasma duration	1-15 min

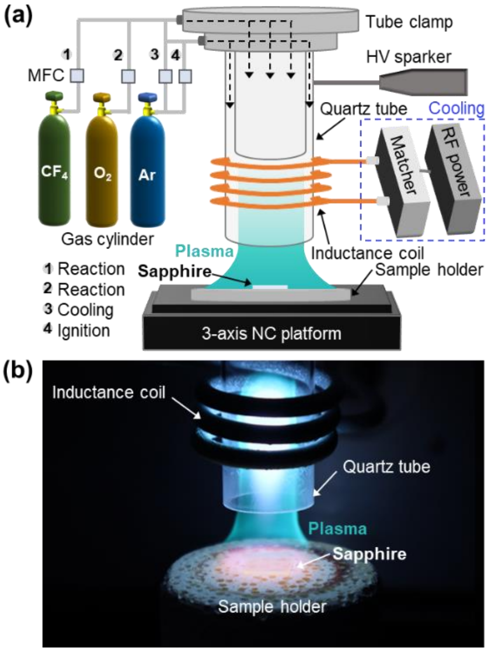

Fig. 1. Atmospheric pressure ICP for the polishing of sapphire. (a) Schematic diagram of ICP setup. (b) Optical image of ICP torch.

Before using our plasma to etch sapphire, we firstly conduct plasma diagnostics to understand its properties. Fig. 2(a) shows the sapphire surface average temperature variation with the RF power from 500 to 1000 W, which is measured by an infraction imager (FLIR T660). It can be seen that the temperature substantially rises with increasing RF power. From 500 to 700 W, the temperature is always below 800 ℃, and the increase rate of temperature is relatively small. However, once the RF power increases from 700 to 800 W, the temperature would dramatically increase from 786 ℃ to 1384 ℃. At 1000 W, the temperature can be as high as 1791 ℃. It is believed that the temperature at 800 W is high enough to sublimate the major etching reaction product, namely, AlF_3 with the melting point of 1291 ℃ [9]. Also, it can be found that the temperature distribution on the sapphire surface is quite uniform, according to the inserted image in Fig. 2(a).

Fig. 2(b) shows the typical optical emission spectroscopy (OES, Ocean Optica USB4000) of ICP at 800 W. Since Ar gas is used as ignition gas in this study, many strong peaks corresponding to the activated Ar can be found at 420.7 nm and from the range of around 700 to 830 nm. With the addition of CF_4, strong peaks related to C (247.7 nm), C_2 (471.2, 516.1, 550.8, and 557.7 nm), and CF_x (358.5 and 387.2 nm) can also be identified, indicating the dissociation of CF_4 and the generation of F radicals [10]. It is believed that these F radicals with strong oxidation potential possess the ability to etch the sapphire substrate. Besides, an oxygen-related peak at 843.6 nm can also be observed. Herein, the addition of O_2 in the reaction gas is to promote the dissociation of CF_4 [10]. Also, the peak at 604.5 nm is identified to from activated N_2, which can be attributed to the mixing of ambient air into the plasma.

Based on the above temperature measurement and OES results, it is safe to say that our ICP indeed shows not only high temperature but also high radical density features. The high-density F radicals can efficiently etch the sapphire, and the high temperature reaction atmosphere makes it possible for products to sublimate from the substrate. Thus, using our ICP to process sapphire is promising.

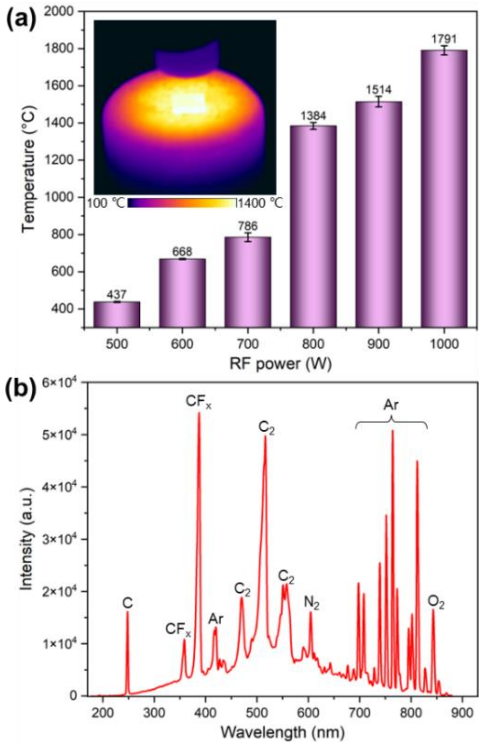

Fig. 2. Plasma diagnostics. (a) Sapphire surface average temperature variation. The inset is the temperature distribution image at 800 W. (b) OES of ICP at 800 W.

3. PASE mechanism for sapphire

Compared with the CMP-based methods that always involve the first surface modification and subsequent mechanical removal, our PASE is a non-contact chemical removal process. The etching process of sapphire can be described as

$$CF_{4(gas)} + O_{2(gas)} + Al_2O_{3(solid)} \rightarrow AlF_{3(gas)} + CO/CO_{2(gas)}.$$

Fig. 3 shows the underlying mechanism of PASE for sapphire. As can be seen in Fig.3 (a), the polishing process of rough sapphire surface can be regarded as the material removal in both the horizontal and vertical directions. The removal in horizontal (vertical) direction is indeed the etching of surface atoms at the step (terrace), where the etching rate is labelled as V_S (V_T). Because the surface atoms at the step always possess more dangling bonds than that at the terrace, V_S is generally larger than V_T. At elevated temperature, the etching rate difference can be greatly enlarged ($V_T << V_S$). This temperature-enhanced selective etching effect has already been proved in our previous study [10]. With the selective etching process going on, all steps on the surface can be removed, and an atomically smooth surface can be consequently obtained.

Fig. 3(b) shows the polishing process of sapphire at atomic scale via PASE. In theory, a perfect sapphire surface without any missing and extra atoms can be formed ultimately.

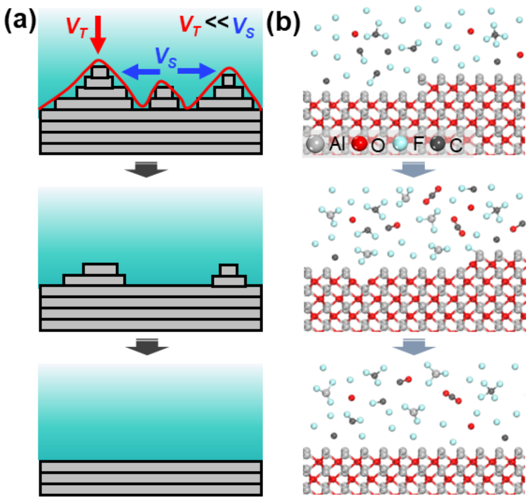

Fig. 3. PASE mechanism for sapphire. (a) Schematic diagram of the polishing process. (b) Atomic-scale surface atoms removal process.

4. Experimental results and analyses

According to the temperature measurement result shown in Fig. 2(a), the sapphire surface average temperature can reach as high as 1384 ℃ with the RF power of 800 W, under which the product AlF_3 could be removed in gaseous form. Thus, we firstly explore the etching process of sapphire at 800 W. Fig. 4 shows the surface morphology and profile changes of sapphire during the etching process, and these results are obtained by a scanning white light interferometer (SWLI, Taylor Hobson, CCI). Herein, we start with a sliced sapphire (0001) substrate with the *S*a roughness of 1223 nm and the peak-to-valley (PV) of 6.66 µm, as shown in Fig. 4(a). After one-minute etching (Fig. 4(b)), the *S*a roughness is decreased to 466.4 nm, and the PV along the selected profile is 2.57 µm. Significantly, some pits can be observed on the surface, demonstrating the etching reaction between sapphire and radicals in our plasma. Then, after five-minute plasma irradiation (Fig. 4(c)), the selective etching effect is greatly obvious, which can be understood from the noteworthy decrease of PV (145.44 nm) and the expansion and overlap of etching pits. Under this circumstance, the *S*a roughness can be reduced to the nanometre level with the value of 34.47 nm. Further, with the extension of plasma duration to 10 min, an atomically smooth sapphire surface with the *S*a roughness of 0.194 nm is obtained, as shown in Fig. 4(d). Since all step structures forming the rough surface are removed through PASE, the final PV can be at atomic scale with the value of only 1.50 nm. Therefore, it can be concluded that our PASE method has the ability to rapidly fabricate atomic-scale smooth sapphire surface.

We further adopt MRR to quantitatively evaluate the polishing efficiency of PASE for sapphire. Herein, MRR is calculated based on the following equation,

$$MRR = \frac{\Delta m}{\rho S t},$$

where Δm means the mass loss before and after PASE, ρ is the density of sapphire (ρ = 3.98 g/cm^3), S is the surface area of sapphire, and t is the plasma duration. At 800 W, MRR is calculated to be 21.99 µm/min; when the RF power increases to 1000 W, MRR could reach 40.79 µm/min, which should be around 750 times larger than that recently reported in the literature [3]. It is believed that MRR could be further improved by optimizing the experimental conditions, for example, increasing the flow rate of CF_4.

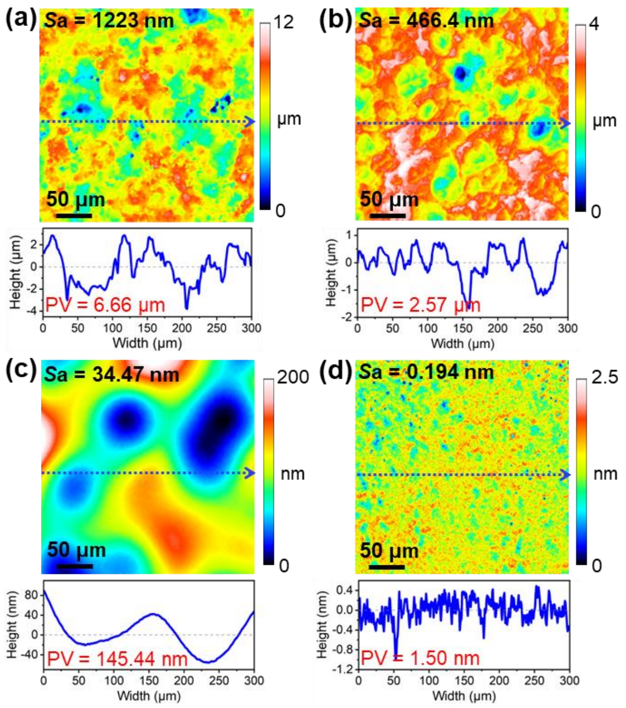

Fig. 4. Surface morphology and profile changes of sapphire during PASE at 800 W. (a) As-received sapphire. (b) 1 min. (c) 5 min. (d) 10 min.

Fig. 5(a) shows the atomic force microscope (AFM, Bruker Dimension Edge in tapping mode) image taken at the PASE-treated sapphire surface at 800 W for 10 min. Clearly, the *S*a roughness in a 10 µm × 10 µm area could be 0.084 nm, which is far smaller than most of the results reported in the literatures [1-8]. We further extend the plasma duration to 15 min and find that the *S*a roughness is still just below 0.1 nm (Fig. 5(b)), indicating that the ultimate sapphire roughness in PASE might be around 0.1 nm. In addition, we use high resolution transmission electron microscopy (HR-TEM, FEI Titan Themis 200) to study the subsurface atomic-scale features of the polished sapphire, and the result is shown in Fig. 5(c). Obviously, all surface and subsurface atoms are regularly arranged, and no subsurface damage can be observed. In fact, the subsurface damage layer caused by the mechanical process on the as-received sapphire substrate would be rapidly removed in PASE, and our PASE would not introduce any new damage as it is a completely chemical etching process without any mechanical action. Hence, it is safe to that PASE is indeed a highly-efficient, damage-free, and atomic-scale surface smoothing technology for sapphire.

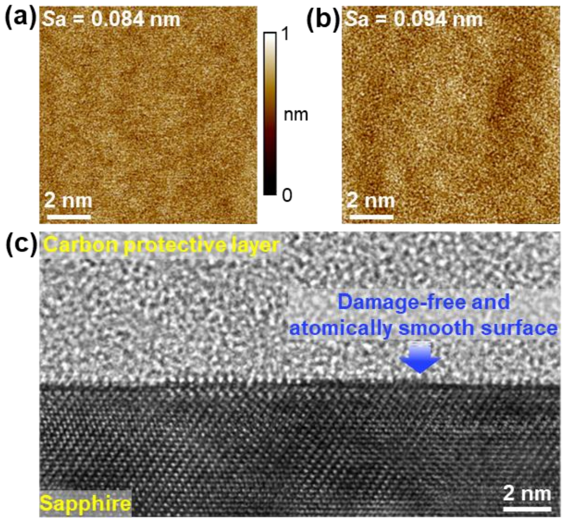

Fig. 5. Atomic-scale surface and subsurface features of sapphire after PASE. AFM images of sapphire treated at 800 W for (a) 10 min and (b) 15 min. (c) HR-TEM image of the polished sapphire.

5. Conclusions

In this study, we propose a highly-efficient plasma-based smoothing method, namely, PASE, to fabricate damage-free and atomically smooth sapphire (0001) surface. The underlying mechanism of PASE is the selective etching of surface atoms at the step structures, where these surface atoms should have more dangling bonds than that at the terrace. We find that after ten-minute PASE treatment at 800 W, an atomic-scale smooth sapphire (0001) surface with the *S*a roughness of 0.084 nm can be obtained. The HR-TEM result strongly demonstrates that no damage can be found on the sapphire after PASE. Compared with CMP-based methods, our PASE can achieve not only the atomic-scale surface roughness but also the extremely high efficiency. We believe that PASE would greatly enrich the atomic-scale manufacturing technology for sapphire, and also promote its application in optics and semiconductors.

6. References

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