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Surface reconstruction of sapphire at the atomic scale via chemical-physical tuning of atmospheric plasma

Hui Deng[a,*], Yongjie Zhang[a,b], Jianwen Liang[a], Xinquan Zhang (2)[c]

[a] Department of Mechanical and Energy Engineering, Southern University of Science and Technology. No. 1088, Xueyuan Road, Shenzhen, Guangdong 518055, China
[b] Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117551, Singapore
[c] School of Mechanical Engineering, Shanghai Jiao Tong University, Shanghai, 200240, China

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ABSTRACT

Atomic surface manufacturing is strongly required for cutting-edge applications in semiconductor and quantum engineering but suffers from the limited surface accuracy of conventional abrasive finishing processes. In this article, surface reconstruction via chemical-physical tuning of atmospheric plasma is proposed for atomic surface manufacturing of single-crystal materials. An ultrasmooth surface of sapphire with *Sa* 0.06 nm can be achieved through atom-selective etching enabled by the chemical mode of plasma. A uniform step-terrace structure can be formed by atomic reconstruction through the physical mode of plasma. This study provides a new strategy for atomic surface manufacturing of single-crystal materials.

1. Introduction

In the semiconductor, quantum engineering and advanced optics fields, an atomically smooth surface is always desirable to realize excellent device performance [1]. For example, the low loss and uniform dielectric properties of sapphire make it an ideal substrate for superconducting quantum circuit applications [2]. Generally, a perfect sapphire surface with the fewest missing or extra atoms is preferred for device fabrication. Currently, chemical mechanical polishing (CMP) has been widely applied for ultrafine polishing of single-crystal substrates [3,4]. However, achieving an atomically perfect sapphire surface through CMP is still difficult. The material removal in CMP is based on abrasion in nature; hence confining the material removal to the desired atom sites is challenging since the abrasives are giant and randomly moving [3].

Manufacturing is rapidly developing and advancing towards atomic and close-to-atomic scale manufacturing (ACSM) [5]. For the manufacturing of ultrasmooth surfaces with atomic precision, various approaches with the assistance of chemical reactions were proposed. Soft abrasive polishing combined with surface modification by plasma was developed and applied to wide bandgap semiconductors [6,7]. Atomic-scale smoothing of glass and silicon with inorganic tools was realized by dehydration reactions [8]. Shear-induced mechano-chemical reactions have been successfully adopted for single Si atom layer removal [9]. The core of atomic surface manufacturing is not only the fabrication of a sufficiently smooth surface with atomic-level roughness but also the regulation of surface atom arrangement. Through cutting-edge ACSM methods, fabrication of surfaces with an ultimate *Sa* roughness below 0.1 nm is already possible [6–9]. However, tuning of the atomic step-terrace structure is considered challenging and has not yet been realized.

In this paper, we propose a surface reconstruction method via chemical-physical tuning of atmospheric plasma. The surface reconstruction mechanisms are discussed. An inductively coupled plasma system with chemical-physical tuning function is developed and applied to sapphire. The surface reconstruction process enabled by the chemical and physical modes of plasma is studied. The proposed process is further verified with other single-crystal materials, such as SiC and Ga_2O_3. This paper thus provides a new strategy for atomic surface manufacturing.

2. Concept and experimental setup

The dissociation/ionization in plasma is always accompanied by radical generation, so plasma has a strong chemical activity, which enables its various applications like etching, modification, and deposition. The chemical interactions between plasma and surfaces have been widely studied, while the physical interactions are seldom reported. In this paper, atomic surface manufacturing is realized using a chemical-physical tuneable plasma.

The plasma tuning process to achieve an atomic surface (chemical mode) and a step-terrace surface (physical mode) is shown in Fig. 1 (a). Through real-time control of the plasma gas supply and radio frequency (RF) power under the premise of plasma diagnostic feedback, the transition between the plasma chemical and physical working modes can be realized. In the chemical working mode, the atom-selective etching effect, in which surface atoms in different bonding states are selectively removed, can be realized by Ar-CF_4—O_2 plasma with proper input conditions. The surface atoms with the most

* Corresponding author.
E-mail address: dengh@sustech.edu.cn (H. Deng).

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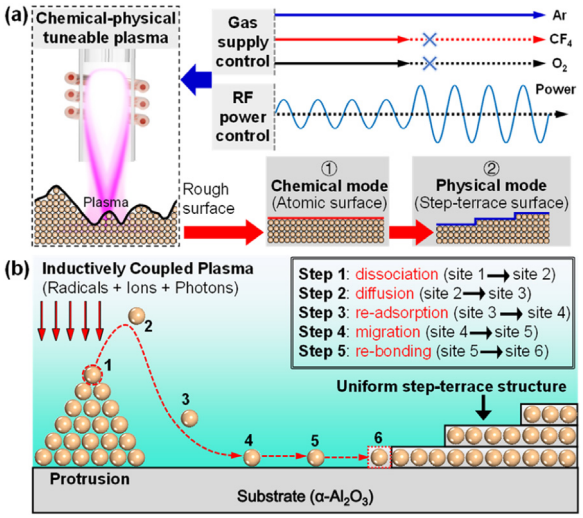

Fig. 1. (a) Schematic of the plasma tuning process to achieve an atomic surface (chemical mode) and a step-terrace surface (physical mode). (b) Schematic of the surface atomic reconstruction process.

dangling bonds will be etched firstly, and a perfect surface with all atoms regularly arranged will eventually be obtained [10].

However, if the plasma is changed to the physical mode, then rearrangement of surface atoms is realized, and a uniform step-terrace structure can be formed, as shown in Fig. 1(b). Pure Ar plasma delivers energy to the surface through particle collisions and photon radiation. Atoms at surface protrusions dissociate, diffuse and then adsorb on the surface, followed by migration and rebonding at low-energy sites, and release energy. This damage-free process occurs in an atmospheric environment, and it is a very efficient and scalable new scheme for the manufacture of atomic step-terrace structures.

An atmospheric inductively coupled plasma (ICP) setup was developed, as shown in Fig. 2. The setup consists of plasma ignition, plasma working mode tuning and plasma diagnostic systems. The

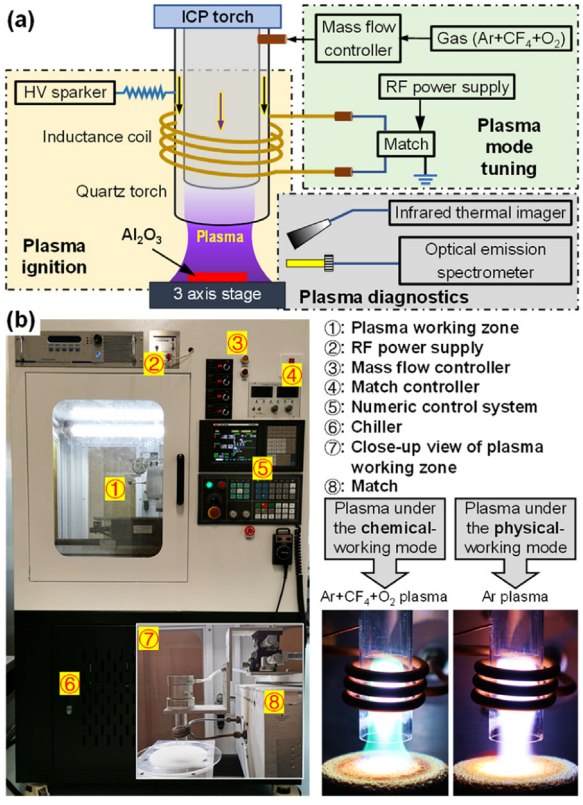

Fig. 2. (a) Schematic of the ICP setup with a chemical-physical tuning function. (b) Photo and configuration of the experimental setup.

plasma ignition part includes a high-voltage (HV) sparker, an inductance coil, and a plasma torch assembled from two concentric quartz tubes. Plasma mode tuning is realized by precise and instantaneous gas supply control using mass flow controllers (MFC), and the RF power is also regulated for temperature control in both the chemical and physical modes of the plasma. Plasma diagnostics are conducted using an infrared thermal imager and an optical emission spectrometer. Additionally, there is a 3-axis numerical control platform, on which the substrates to be processed can be mounted. Fig. 2(b) shows a photo of the experimental setup, where several significant components are labelled in the picture.

Based on this setup, atmospheric plasma with tuneable composition and temperature is generated. Additionally, optical images of Ar-CF_4—O_2 plasma and pure Ar plasma are shown in Fig. 2(b). They present totally different colours, indicating their different radical compositions. The related experimental parameters are summarized in Table 1. When the plasma is working under the chemical mode, surface atoms are efficiently removed by chemical etching using Ar-CF_4—O_2 plasma ($Al_2O_3(s) + CF_4(g) + O_2(g) \rightarrow AlF_3(g) + CO/CO_2(g)$). When the plasma is tuned to the physical mode using pure Ar plasma, chemical etching stops, and the surface is reconstructed in the atomic-scale through diffusion, migration and re-bonding of surface dissociated atoms.

Table 1
Experimental parameters.

Parameters	Values
Specimen	α-Al_2O_3 (0001): 10 × 10 mm^2
Frequency of power	27.12 MHz
Power input	500–1000 W
Flow rates of gas	Carrier/Cooling Ar gas: 1.5/18 L/min Reactive gas: 20 mL/min O_2, 60 mL/min CF_4
Tube diameter	Inner tube: 14/16 mm inner/outer diameter Outer tube: 18/20 mm inner/outer diameter
Plasma jet distance	15 mm (working distance)
Time	0.5–15 min

The radical composition and density in plasma was detected using an optical emission spectrometer (OES, Ocean Optics USB2000). Temperature distribution of the substrate surface during plasma processing was mapped by an infrared thermal imager (FLIR T660). The surface roughness was measured by a white light interferometer (WLI, Taylor Hobson, CCI). The topography of the atomic surface and the step-terrace surface was measured using an atomic force microscopy (AFM, Bruker Dimension Edge). AFM measurements were carried out under the tapping mode using a silicon micro cantilever (Olympus, OMCL-AC160TN-R3). The tip has radius of 7 nm, a resonant frequency of 300 kHz and a spring constant of 26 N/m. Surface morphology evolution during plasma processing was recorded using a laser scanning confocal microscopy (LSCM, Keyence VK-X1000). X-ray photoelectron spectroscopy (XPS, PHI 5000 Versaprobe Ⅲ) was used for validation of surface chemical composition.

3. Results and discussion

3.1. Plasma diagnostics

One reason for the selection of ICP rather than capacitively coupled plasma is that ICP under atmospheric pressure possesses the superior properties of high temperature and radical density. Plasma diagnostics by measuring of OES spectrum was conducted to qualitatively explore the composition of radicals in Ar-CF_4—O_2 plasma and pure Ar plasma.

As shown in Fig. 3(a), the Ar-CF_4—O_2 plasma has many strong peaks which are corresponded to C, C_2, CF_x, and O_2 species, apart from the Ar peaks, indicating that CF_4 molecules were dissociated and active F atoms with strong oxidation potential were generated. Peaks originating from F atoms were not detected owing to the short lifetime of excited F atoms. It is worth mentioning that O_2 was added to the chemical mode plasma, aiming to promote the dissociation of

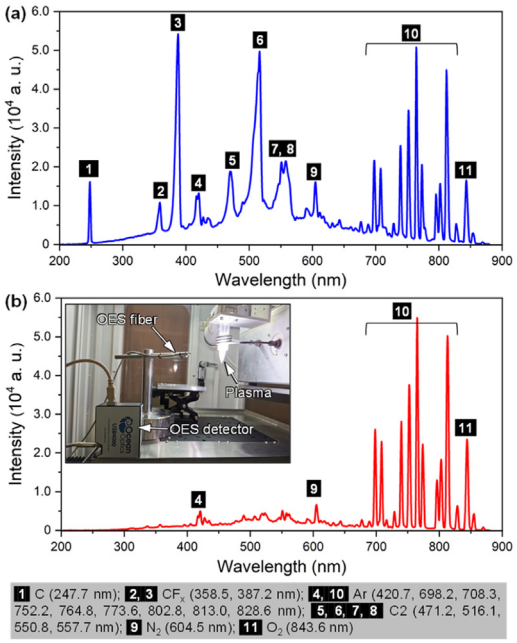

Fig. 3. OES spectra of the plasma working under the chemical (a) and physical (b) modes.

CF_4, and the CF_4/O_2 ratio played an important role in achieving the atom-selective etching effect [10]. In comparison, no peaks related to C, C_2, and CF_x species can be found in the pure Ar plasma, as shown in Fig. 3(b), demonstrating that the pure Ar plasma does not possess any etching ability. For the Ar plasma, weak N_2 and O_2 peaks can also be observed, and these peaks are considered to originate from the ambient air. However, they will not induce any chemical reactions owing to the strong chemical inertness of sapphire. The OES spectra demonstrate the feasibility of tuning the plasma from the chemical to physical mode.

3.2. Atomic surface manufacturing by chemical-plasma

Under the chemical working mode using Ar-CF_4—O_2 plasma, the atom-selective etching effect can be realized under optimized CF_4/O_2 ratio and RF power [11]. As shown in Fig. 4(a), a sliced rough sapphire surface could be quickly smoothed by plasma etching. After 2 min of plasma etching, disordered micron-size step structures can be clearly observed. Owing to the atom-selective etching effect, atoms at step edges have a higher etching priority than terrace atoms leading to the generation of disordered step structures. The steps are preferentially etched; thus, the step structure gradually disappears. Once the duration reaches 5 min, the steps are all removed, and an atomic surface is formed.

Fig. 4(b) shows the evolution of the *Sa* roughness during plasma etching. The as-received rough substrate with an average *Sa* of 1116 nm would be rapidly converted into an etched surface with a *Sa* roughness of approximately 221 nm within 2 min of treatment. At 5 min, the *Sa* roughness can be further decreased to 31.74 nm. Then, after 10 min of atom-selective etching process, an ultrasmooth sapphire surface with 0.21 nm *Sa* was formed. It is also revealed that a further increase in the duration would not effectively reduce the *Sa* roughness.

Evolutions of the material removal rate (MRR) and surface temperature at different plasma powers were also evaluated, as shown in Fig. 4(c). Herein, the MRR was calculated from the weight change after atom-selective etching. Both the MRR and temperature increase with increasing RF power from 500 to 1000 W. The above results demonstrate that the MRR is strongly dependent on the temperature, which can be explained by the Arrhenius equation, where a temperature rise would undoubtedly lead to the increase in rate constant for the atom-selective etching reaction.

Furthermore, atom-selective etching was compared with the widely used CMP and modified CMP methods, as shown in Fig. 4(d), where all *Sa* roughness values were measured by AFM [12–15].

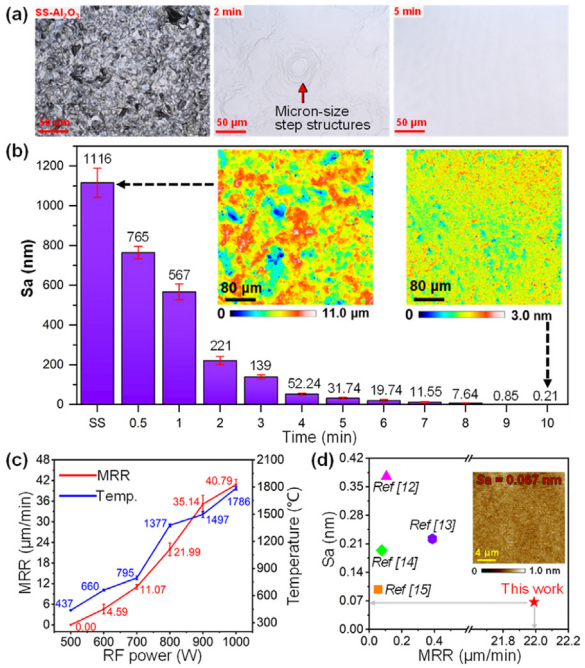

Fig. 4. (a) Surface morphology during atom-selective etching. (b) Surface roughness evolution. (c) MRR and temperature for different plasma powers. (d) Comparison with CMP approaches.

Apparently, our method shows the largest MRR (21.99 μm/min) and smallest *Sa* roughness (0.067 nm/20 μm × 20 μm). This *Sa* roughness value is believed to be the lowest surface roughness reported to date, to our knowledge.

3.3. Step-terrace surface manufacturing by physical-plasma

Once the plasma working mode is tuned from the Ar-CF_4—O_2 plasma-enabled chemical mode to the physical mode using pure Ar plasma, surface reconstruction will occur, and an atomic step-terrace structure will be formed. Fig. 5 shows the tuning of the step-terrace structure using the physical mode plasma (800 W). After one minute of surface reconstruction, a uniform step-terrace structure with 0.25 nm of step height, corresponding to one bilayer of sapphire, can be obtained. Moreover, it is clear that the longer the process duration, the higher the step height, resulting in an increase in the *Sa* roughness. Note that the step-terrace structure is stabilized after 20 min, leading to a final *Sa* roughness of approximately 1.0 nm and a step height of 4.0 nm. Thus, it is concluded that tuning of the step-terrace structure on sapphire is possible using the physical mode plasma.

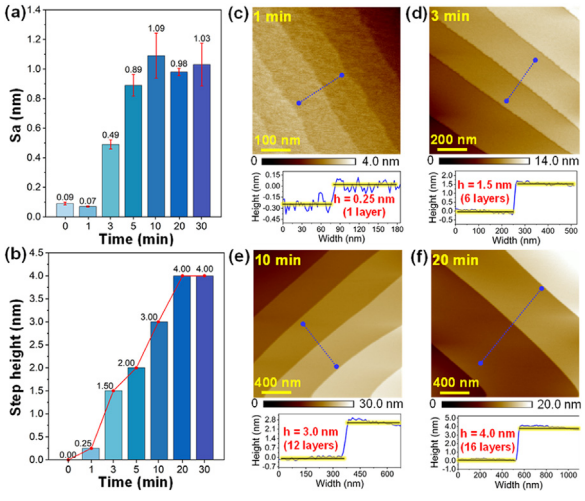

Fig. 5. Tuning of the step-terrace structure using pure Ar plasma.

To prove that the surface reconstruction process forming the step-terrace structure is a purely physical process, the chemical bonding state of the sapphire surface before and after the reconstruction process was analysed by XPS, and Fig. 6 shows the results. The wide scanning spectrum prove that there is no difference in the distribution of atomic valence states on the surface before and after plasma treatment. For the high-resolution scanning, all peaks were calibrated by the C1s peak at 284.8 eV originated from carbon contamination. From the characteristic peaks of Al2p, O1s, C1s, and Ar2p, it can be confirmed that the physical mode plasma will not form new chemical components, and the implantation of Ar from the plasma is also negligible. It is also notable that the substrate weight was measured as constant even after 30 min of plasma processing, proving that the surface reconstruction enabled by the physical mode plasma is a near-net process.

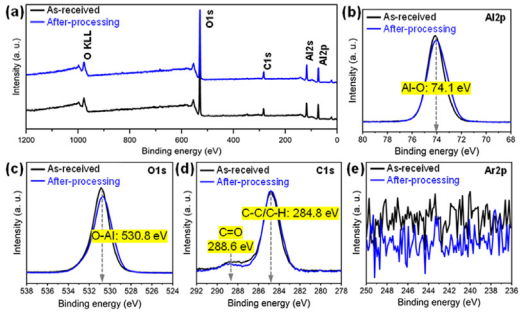

Fig. 6. XPS spectra of the as-received and plasma-processed Al_2O_3 surface. (a) the survey scan. (b) Al2p. (c) O1s. (d) C1 s. (e) Ar2p.

3.4. Surface reconstruction of 4H-SiC and β-Ga_2O_3

The general applicability of the proposed atomic-scale surface reconstruction method was verified with 4H-SiC (0001) and β-Ga_2O_3 (−201), as shown in Fig. 7. Similarly, damaged and rough 4H-SiC (0001) and β-Ga_2O_3 (−201) surfaces with *Sa* roughness values of 15.1 nm and 11.6 nm, respectively, were used. Then, with the plasma first working in the chemical mode, atom-selective etching under different conditions was separately conducted for 4H-SiC (600 W, 10 min) and β-Ga_2O_3 (900 W, 0.5 min), after which the *Sa* roughness values were reduced to 0.056 nm and 0.050 nm, demonstrating that atomically smooth surfaces of 4H-SiC and β-Ga_2O_3 were obtained. Then, the plasma was tuned to the physical mode, and surface reconstruction occurred for 4H-SiC (1000 W, 2 min) and β-Ga_2O_3 (1000 W, 10 min). Clear and uniform step-terrace structures can also be formed on these two substrates, demonstrating that surface reconstruction via chemical-physical tuning of plasma can be used as a general approach for highly efficient manufacturing of atomically smooth surfaces of single-crystal materials.

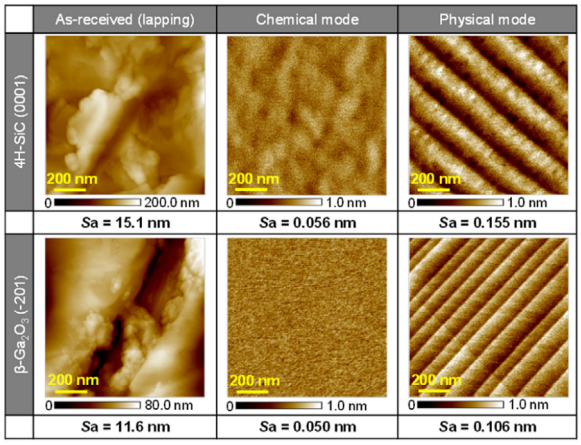

Fig. 7. AFM images of 4H-SiC (0001) and β-Ga_2O_3 (−201) processed by plasma working in the chemical and physical modes.

4. Summary

Surface reconstruction via chemical-physical tuning of atmospheric plasma was proposed to realize highly efficient manufacturing of atomically smooth surfaces of single-crystal materials. An ICP-plasma system with a plasma mode tuning function was developed and verified by plasma diagnostics. An atomic surface of sapphire with a 0.067 nm Sa was obtained by atom-selective etching using chemical mode plasma. Formation and tuning of the step-terrace surface of sapphire was carried out under the plasma physical mode. The general applicability of the proposed atomic-scale surface reconstruction method was further validated with 4H-SiC and β-Ga_2O_3.

This study presents a novel and effective ACSM method, which has the potential to be applied by industry in producing atomically smooth surfaces with a large wafer-scale area.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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