A sapphire nanostructure fabrication method based on friction-induced hydroxyl dehydration condensation

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Single crystal sapphire is an important photoelectric material, which shows broad application prospects in various fields such as precision optics and epitaxial growth. Sapphire with nanostructures has received extensive attention due to its unique properties. However, due to the high hardness and brittleness of sapphire, it is difficult to obtain sapphire nano-structures by mechanical processing. In this study, a method for preparing sapphire nanostructures based on friction-induced hydroxyl dehydration condensation is proposed. The friction between SiO_2 and sapphire causes the dehydration and condensation of hydroxyl groups to form a Si-O-Al bonding bridge. The atoms on the sapphire surface move under the pull of the Si-O-Al bonding bridge during the friction process. Due to the miscut angle on the sapphire surface, the atoms have a tendency of step arrangement, which leads to a gradient of the surface energy barrier. The Si-O-Al bonding bridge breaks at the higher surface energy barrier, resulting in the accumulation of atoms on the surface of sapphire and the formation of nano-step structure. The result of EDS shows that the atoms on the surface of sapphire are transferred to SiO_2 in one direction, while the atoms of SiO_2 are not transferred to sapphire. Compared with other preparation methods of sapphire nanostructures, this method has the advantages of low cost, easy operation and environmental friendliness, which provides a new idea for the preparation of sapphire nanostructures.

1. Introduction

Single crystal sapphire (α-Al_2O_3), is widely used in the field of precision optics, epitaxial growth, and electronic devices, owing to its extremely high hardness (Mohs hardness: 9) [1], stable chemical properties, excellent optical and thermal properties [2]. Sapphire with nanostructures has attracted much attention due to its unique excellent properties. In the field of epitaxial growth, nano-patterned sapphire substrates can induce epitaxial lateral overgrowth, thereby reducing the threading dislocation density (TDD) of the epitaxial film and improving the performance of LED devices [3]. In addition, the nano-structured sapphire surface is usually oleophobic or hydrophobic, which can be used in scenes such as optical windows and mobile phone screens to achieve self-cleaning of the sapphire surface [4]. However, due to the high hardness and brittleness of sapphire, it is difficult to obtain nano-structured sapphire by mechanical processing.

Currently, the methods of achieving sapphire nanostructures mainly include chemical etching, laser processing and ion beam processing. Chen et al. developed a method to obtain sapphire nanopillars with vertical sidewalls by nanoimprint, SiO_2 masking and ICP etching, which is expected to be used for large volume manufacturing of GaN LED light extraction applications [5]. Ngo et al. produced a sapphire surface with a grid structure by a combination of laser surface ablation and heat treatment. The light transmittance and hydrophobicity tests showed that the surface was superhydrophobic and the light transmittance reached more than 75 %. It is expected to be applied to self-cleaning optical windows[6]. Jelmakas et al. fabricated arrays of square and rectangular trenches on the surface of sapphire by focused ion beam micromilling, which effectively reduced the TDD of GaN ELO layer[7]. Although the above methods can be utilized to achieve the sapphire nanostructures manufacturing, they all have corresponding drawbacks. The chemical etching method has serious environmental pollution, and the preparation process is complicated. Laser processing can accurately produce nanostructures on the surface of sapphire, but it will inevitably cause thermal damage. Ion beam processing can obtain nanostructures accurately and without damage, but the processing efficiency is very low and the cost is very high [8].

In this study, we proposed a new method for the preparation of sapphire surface nanostructures based on friction-induced hydroxyl dehydration condensation. The hydroxyl dehydration condensation reaction is induced by the friction of spherical SiO_2 on the sapphire surface, and the Si-O-Al bonding bridges form at the tribological interfaces, which provides tensile stress during the relative motion process, resulting in the movement of the sapphire surface atoms. The Si-O-Al bonding bridge breaks at a higher surface energy barrier, resulting in the accumulation of atoms on the sapphire surface, and then form nanostructures. We analyzed the material transfer mode of the friction process by SEM and EDS, and proposed the possible mechanism of this method. Compared with other ways, this method has extremely low processing cost, simple operation and environmental friendly.

2. Experimental details

2.1 Experimental setup

Fig.1(a) shows the optical image of the experimental device used in this study. The device consists of four main parts: loading system, tank, motion platform, water supply system (two pumps, filter). The loading system is used to provide the load required for processing. The tank provides a water condition and fixes the sapphire. The motion platform drives the tank to reciprocating motion. The water supply system stably provides pure water and filters the debris. The schematic diagram of the loading system and the tank is shown in Fig. 1(b). The loading system is composed of a lever device. Firstly, the approximate load is obtained by adding weights, and then the position of the counterweight is adjusted to obtain the accurate load. The pure water provided by the outlet pipe continuously scours the tribological interfaces, and takes away the debris from the tribological interfaces. There is a drainage hole on one side of the tank, which is lower than the surface of sapphire, so that the debris can be discharged from the tank in time. More details of the processing parameters are shown in Table 1.

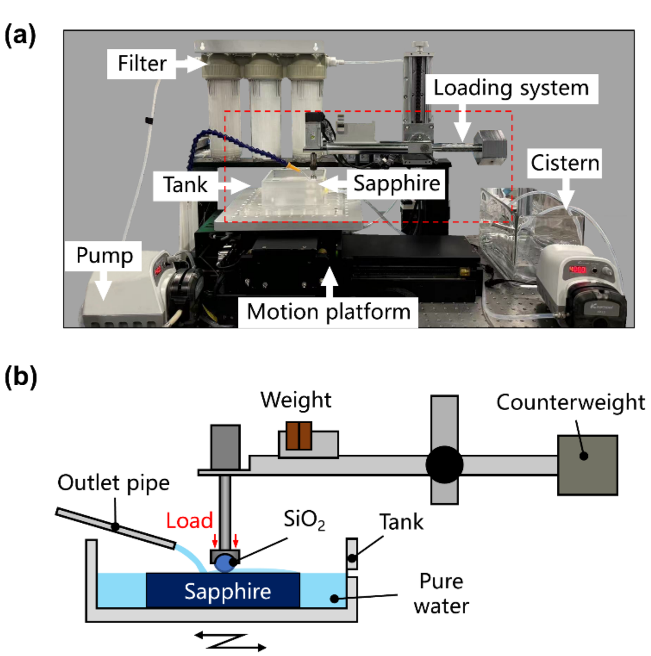

Fig. 1 Experimental device. (a) Optical image of experimental device. (b) Schematic diagram of loading system and tank.

Table 1. Processing parameters.

Parameters	Values
Sample	Sapphire (0001) substrate in 10 mm × 15 mm
Load	2 N
Distance	5 mm
Speed	50 mm/min
Flow rate	900 ml/min
Time	30 min

2.2 Materials and characterization

The sliced sapphire substrates (10 mm × 15 mm) with C-plane were used in this study, and the surface is polished by CMP. The grinding tool was SiO_2 ball with a diameter of 8 mm. The surface morphology of the friction region was obtained by an atomic force microscopy (AFM, Bruker Dimension Edge) in the tapping mode. The morphology and chemical composition of the friction region of sapphire and SiO_2 were examined by scanning electron microscope and energy dispersive spectrometer (SEM and EDS, Apreo2 S Lovac).

3. Results and discussion

3.1 Morphology and composition analysis of nanostructures

Fig. 2 shows the AFM images of sapphire nanostructures prepared based on friction-induced hydroxyl dehydration condensation. Fig. 2(a) is the sapphire surface before friction. The surface is polished by CMP, which is flat without scratches, and the RMS roughness is 0.130 nm. The surface morphology after friction is shown in Fig. 2(b). It can be seen that the surface after friction is covered with periodic nano-step structures. The length of each step is about 800 nm, the width is about 300 nm, and the height is about 10 nm. Each nano-step has similar gradients and consistent directions. After calculation, it is found that the inclination angle of the nano-step is about 0.7°, so it is speculated that the formation of the nano-step is related to the miscut angle of the sapphire (<1°).

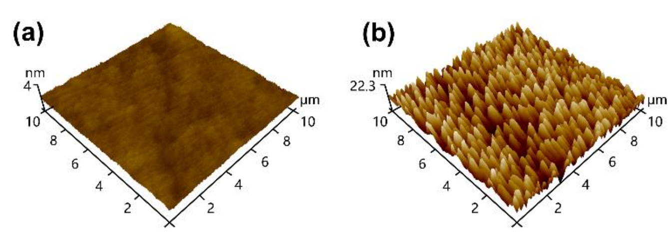

Fig. 2 AFM images of sapphire before and after friction. (a) Surface morphology before friction. (b) Nano-step structures after friction.

In order to understand the generation process of nano-step structures, the friction region of sapphire and SiO_2 is detected by SEM and EDS. The SEM image of the friction region of SiO_2 is shown in Fig.3 (a). Because the hardness of SiO_2 is significantly lower than that of sapphire, there is a very obvious circular wear scar in the friction region of SiO_2. EDS detection is performed on this area, and the result is shown in Fig.3 (b). The elements in the friction region are composed of Si, O and Al. Si and O are the main components of SiO_2, and Al comes from the material transferred from sapphire to SiO_2 during the friction process. In addition, there is more Al at the edge of the wear scar, while the distribution of Al inside the wear scar is dispersed. Therefore, it can be considered that the Al atoms on the sapphire surface are first transferred to the inside of the SiO_2 wear scar, and then pushed to the edge of the wear scar during the reciprocating friction.

The SEM image of the sapphire friction region is shown in Fig 3 (c). Because the friction region is difficult to find by SEM, two symmetrical locating lines are processed by laser on both sides of the friction region before SEM detection. Due to the extremely high hardness of sapphire, wear scar cannot be observed in the friction region under a large field of view. The EDS elemental mapping images results of the sapphire friction region is shown in Fig.3 (d). The elements in the friction region are composed of Al and O, and a small amount of Si is detected at the locating line, while Si is not detected in the friction region. However, the locating line is processed by laser, and there is no Si in the process. Therefore, it can be considered that Si is the error caused by charge accumulation, due to the poor conductivity of sapphire. In summary, in the process of friction between sapphire and SiO_2, the atoms on the surface of sapphire are transferred to SiO_2 in one direction, while the atoms on the surface of SiO_2 are not transferred to sapphire. Since the material transfer in the friction process is achieved by the dehydration and condensation of the hydroxyl groups on the two surfaces to form the Si-O-Al bonding bridge, it can be speculated that the fracture position of the Si-O-Al bonding bridge is on the sapphire side, which may be related to the decrease of the binding energy between the sapphire Al-O bonds after the formation of the Si-O-Al bonding bridge[9].

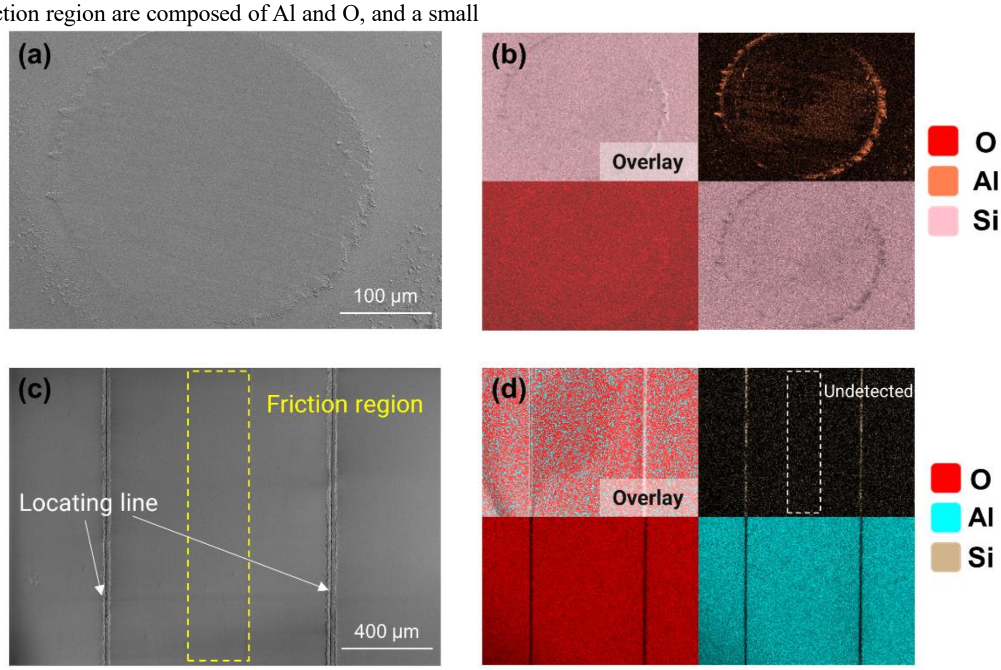

Fig. 3 SEM and EDS results of the friction region of sapphire and SiO_2. (a) SEM image of SiO_2. (b) EDS elemental mapping results of SiO_2. (c) SEM image of sapphire. (d) EDS elemental mapping results of sapphire.

3.2 Preparation mechanism of nanostructures

Fig.4 shows the possible mechanism of the preparation process of sapphire nano-step structures based on friction-induced hydroxyl dehydration condensation. Fig.4 (a) shows the surface state of sapphire and SiO_2 before contact, and the surface of both can react with the moisture in the environment to form Al–OH and Si–OH. Subsequently, when these two surfaces are in contact with each other, the hydroxyl dehydration condensation reaction occurs at the tribological interfaces. After the combination of Si-OH and Al-OH, H_2O is separated and the Si-O-Al bonding bridge is formed (Fig. 4b). Fig. 4(c) shows the friction process after the contact between sapphire and SiO_2 surface. The Si-O-Al bonding bridge has the effect of transmitting tensile stress[10]. During the friction process, it can move the atoms on the sapphire surface and squeeze or stretch the surrounding atoms to move together. Fig. 4(d) shows the process of Si-O-Al bonding bridge detachment from sapphire surface. Due to the miscut angle on the surface of sapphire, there is a gradient of surface energy barrier, so the Si-O-Al bonding bridge is easier to break at the position with higher surface energy barrier and takes away some sapphire atoms. With the repetition of the above process, the sapphire surface material will accumulate at the high energy barrier position, thus forming nano-step structures with inclination angle close to the sapphire miscut angle.

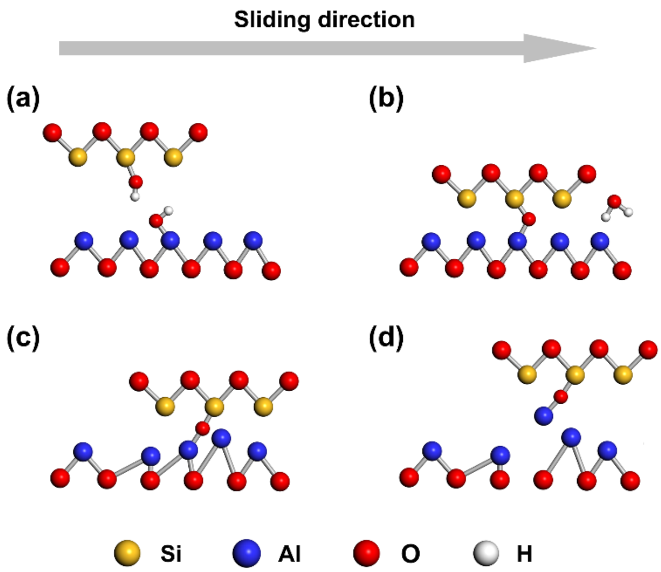

Fig. 4 The possible preparation mechanism of sapphire nano-step structures. (a) Initial state of sapphire and SiO_2 surfaces. (b) The Si-O-Al bonding bridge is formed by the dehydration condensation reaction of hydroxyl groups on the two surfaces. (c) The atoms on the sapphire surface are pulled during the friction process. (d) Si-O-Al bonding bridge fracture and takes away some sapphire atoms.

4. Conclusions

In this study, we propose a new method for preparing sapphire nanostructures based on friction-induced hydroxyl dehydration condensation. The periodic nano-step structures with a height of about 10 nm is successfully prepared on the surface of sapphire by friction experiments. In addition, the chemical composition of the friction region of sapphire and SiO_2 is analyzed by SEM and EDS, and the mechanism of preparing sapphire nanostructures based on friction-induced hydroxyl dehydration condensation is speculated. The Si-O-Al bonding bridge formed by the combination of Si-OH and Al-OH pulls the atoms on the sapphire surface, causing the atoms on the sapphire surface to move and accumulate at the high energy barrier position, thereby forming the nano-step structures. Compared with the existing preparation methods of sapphire nanostructures, this method has the advantages of low cost, easy operation and environmental friendliness. However, the preparation mechanism of nanostructures is still not clear enough, which will become the main research interests in the future.

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