Study on the Influence of Sapphire Crystal Orientation on Its Chemical Mechanical Polishing

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Abstract: Sapphire has been the most widely used substrate material in LEDs, and the demand for non-C-planes crystal is increasing. In this paper, four crystal planes of the A-, C-, M- and R-plane were selected as the research objects. Nanoindentation technology and chemical mechanical polishing technology were used to study the effect of anisotropy on material properties and processing results. The consequence showed that the C-plane was the easiest crystal plane to process with the material removal rate of 5.93 nm/min, while the R-plane was the most difficult with the material removal rate of 2.47 nm/min. Moreover, the research results have great guiding significance for the processing of sapphire with different crystal orientations.

Keywords: sapphire; crystal orientation; anisotropy; polishing

1. Introduction

Due to the excellent material properties such as high hardness, good light transmittance, high chemical and thermal stability, sapphire has been widely used in high-end technical fields such as communications, electronics, aerospace, optics, and biological engineering [1–6]. As a typical anisotropic material, sapphire (α-Al2O3) with different crystal planes has different mechanical and optical properties [7]. At present, sapphire is among the most important substrate materials in the LED field [2,8,9]. The C-plane sapphire wafer is currently the most widely used sapphire substrate for GaN growth by major companies [4,10]. The main reason is that the sapphire crystal growth process along the C axis is mature and the finished product is prepared. The cost is relatively low and the physical and chemical properties are stable. However, GaN films grown on some non-C-planes, such as R-plane and M-plane sapphire substrates, are non-polar and semi-polar [11]. Compared with traditional C-plane sapphire barrier crystals, GaN films grown on R-plane or M-plane sapphire could greatly improve the luminous efficiency of the device. Therefore, the demand for high-quality R-plane and M-plane sapphire substrates is increasing. The sapphire crystal planes such as C-, A-, M- and R-plane have attracted more and more attention from researchers and become current research hotspots [12].

Nanoindentation technology is currently the most useful method to explore the mechanical properties at sub-micro and nano-scales [13]. Mao et al. [14] evaluated the elastic–plastic behavior of the C-plane of single-crystal sapphire by using ultra-low nanoindentation loads with a Berkovich indenter. Ma et al. [15] studied the crystallographic orientation effect on the incipient plasticity and stochastic behavior of a sapphire single crystal by spherical nanoindentation. Trabadelo et al. [16] studied the deformation and cracking behavior of sapphire under spherical nanoindentation for suppling and
enriching the existing studies. Manjima Bhattacharya et al. [17] did the research to investigate the interaction of nanoscale damages with static and dynamic contact and induced damages in alumina by using nanoindentation.

Nowadays, lots of researchers have focused on studying the processing performance of sapphire with different crystal orientations. Luo et al. [18] analyzed the material removal mode of three crystal planes in mechanical planarization and revealed the removal mechanism of sapphire substrates. Cheng et al. [19] did the research and reported that the grinding force of the A-plane is higher than that of the C-plane of sapphire in micro slot-grinding experiment. Wang et al. [20] did the experiment by double-sided planetary grinding and found that the crystal orientations with higher Young’s modulus and fracture toughness were more difficult to realize the material removal. Wang et al. [21] did the research on the machinability of the A-plane sapphire under diamond wire cutting in different cutting directions.

However, there are few studies which combine the micro-scale material properties with macro-level processing although a lot of research has been performed to reveal the micromechanical behavior of sapphire by nanoindentation. Therefore, this paper will correlate the nanoindentation experiment with the results of sapphire chemical mechanical polishing and then reveal the nature of the anisotropy characteristics on the sapphire processing results. Apart from that, it will lay a theoretical basis and a significant guidance for the selection of parameters in processing with different crystal orientations.

2. Experimental

2.1. Nanoindentation Experiment

Four crystal orientations (A-plane, C-plane, M-plane, R-plane) sapphire wafers used in the nanoindentation experiment were 2-inch wafers fabricated by Kyropoulos method provided by Tiantong Company (China). The thickness of the sapphire wafer was 430 ± 5 µm, and the radius of the wafer was 25.4 mm. Before the experiment, all wafers were strictly polished and their surface morphology and surface roughness were measured by SuperView W1 Optical 3D surface profiler, which were shown in Figure 1. The nanoindentation experiment was carried out on Agilent Nano Indenter G200, and the temperature during the whole experiment was controlled at a constant value of 20 °C. Hardness and elastic modulus were measured with a standard Berkovich indenter by continuous stiffness module (CSM). The maximum displacement and the strain rate was controlled at 1000 nm and 0.05 s⁻¹. In order to ensure the reliability of the experimental data, the indentation experiments of each crystal plane were repeated 10 times, and six groups of data were randomly selected for statistics from the 10 times.

![Figure 1. Cont.](image-url)
The slurry was chosen as a silica sol with the particle size of 80 nm, the concentration of 10 wt% and the pH of 9.75. In addition, a constant flow rate of 75 mL/min of slurry was maintained during the polishing experiment. Each wafer was ultrasonically cleaned with absolute ethanol and deionized water for 3 min. The surface of the sapphire substrates was evaluated by optical 3D surface profiler (SuperView W1, China) and scanning electron microscopy (SEM; ZEISS SIGMA, Germany). A electronic balance (Sartorius MSA225S, Germany) was used to measure the quality loss of sapphire wafer before and after polishing. In the processing experiment, polyurethane was used as the polishing pad and the rotation speed of the loading plate and the polishing plate was set at 60 rpm and the pressure was 14.51 KPa. The slurry was chosen as a silica sol with the particle size of 80 nm, the concentration of 10 wt% and the pH of 9.75. In addition, a constant flow rate of 75 mL/min of slurry was maintained during the polishing experiment.

3. Results and Discussion

The relationship between the hardness (H) and the indentation depth (h) of the four crystal orientations of sapphire is shown in Figure 3. It was suggested that the experimental data were true and reliable because of the high curve overlap of the six experiments. The hardness value of sapphire with different crystal orientations increased rapidly in range of 0–100 nm of the indentation depth, and then the hardness rapidly decreased to the normal value. Subsequently, the value slowly decreased with increasing displacement.
Figure 3. The hardness as a function of the indentation depth of the four crystal orientations for the (a) A-plane, (b) C-plane, (c) M-plane and (d) R-plane.

As it was shown in Figure 4, the nanoindentation results of the elastic modulus (E) exhibited a good repeatability for the four crystal orientations of the A-plane, C-plane, M-plane and R-plane. The change of the elastic modulus with the indentation depth (h) was similar to the change of the hardness. After a rapid decrease in some range, the numerical change tended to be gentle.

Figure 4. Cont.
was very fast in the initial processing stage. This is because the surface quality of the sapphire workpiece would become better, and the number of rough peaks and the height of the protrusions would gradually decrease, which was equivalent to the gradual decrease in the load acting on the unit area. Therefore, the material removal rate (MRR) slowed down as the processing time increased. Moreover, it could be clearly observed from the figure that the material removal rate of the C-plane was almost faster than the other three crystal planes in the processing time period, and the material removal rate of the R surface was the lowest. There was little difference between the A-plane and the M-plane, but the M-plane was slightly faster than the A-plane. The mean value of the material removal rate of the R surface was the lowest. There was little difference between the A-plane and the M-plane, but the M-plane was slightly faster than the A-plane.

The hardness at the indentation depth of 500 nm was 28.7 ± 0.45 GPa, 24.9 ± 0.55 GPa, 25.9 ± 0.34 GPa, and 29.6 ± 0.56 GPa for the A-plane, C-plane, M-plane and R-plane, respectively. The elastic modulus recorded at the depth of 500 nm was 417.2 ± 4.63 GPa, 402.6 ± 8.24 GPa, 407.8 ± 4.29 GPa, 418.6 ± 4.16 GPa for the A-plane, C-plane, M-plane and R-plane, respectively.

It could be concluded that the hardness value and elastic modulus increased in sequence according to the C-plane, M-plane, A-plane, R-plane from the statistical data.

Figure 5 exhibited the material removal rate (MRR) as a function of the polishing time of the four crystal orientations. The material removal rate of all sapphire wafers with different crystal orientations was very fast in the initial processing stage. This is because the surface quality of the sapphire workpiece in the initial stage was not sufficiently good, and there were a lot of rough peaks with different heights. The material removal rate began to decrease with a period of processing, then stabilized within a certain range as the polishing time continued to extend. As the processing time increased, the surface quality of the sapphire workpiece would become better, and the number of rough peaks and the height of the protrusions would gradually decrease, which was equivalent to the gradual decrease in the load acting on the unit area. Therefore, the material removal rate (MRR) slowed down as the processing time increased. Moreover, it could be clearly observed from the figure that the material removal rate of the C-plane was almost faster than the other three crystal planes in the processing time period, and the material removal rate of the R surface was the lowest. There was little difference between the A-plane and the M-plane, but the M-plane was slightly faster than the A-plane. The mean value of the material removal rate was counted when the MRR became stable in this period. The material removal rate calculated by Formula (1) of the A-, C-, M- and R-plane were 3.85 ± 0.47 nm/min, 5.93 ± 0.84 nm/min, 4.16 ± 0.39 nm/min, 2.47 ± 0.22 nm/min. Therefore, the relationship of material removal rate was approximately as C-plane > M-plane > A-plane > R-plane.

\[
MRR = \frac{\Delta m}{\rho \pi R^2 l} \times 10^7
\]
where MRR is the material removal rate, $\Delta m$ is the mass change of sapphire substrates, $\rho$ is the density of sapphire substrates, $\rho = 3.98 \text{ g/cm}^3$, $R$ is the radius of sapphire substrates, and $t$ is the polishing time.

Figure 5. Material removal rate (MRR) as a function of the polishing time of the four crystal orientations for the A-plane, C-plane, M-plane and R-plane.

Figure 6 exhibits the surface roughness $R_a$ as a function of the polishing time of the four crystal orientations. The initial average surface roughness of the A-, C-, M- and R-plane were 687.242, 654.848, 661.969 and 692.124 nm, respectively. It could be found that the surface roughness of sapphire wafers with different crystal planes decreased rapidly at the beginning of processing. As was the case with the MRR, the initial stage was inadequate.

Figure 6. Surface roughness $R_a$ as a function of the polishing time of the four crystal orientations for the A-plane, C-plane, M-plane and R-plane.

Reaching a certain polishing time, the trend of roughness began to slow down. There was almost no obvious change and the value fluctuated within a certain numerical range. It can be clearly observed from the figure that the roughness improvement of the C-plane is significantly better than the other three crystal surfaces, followed by the M surface.

In addition, further analysis of the processing data revealed that the roughness of the C-plane sapphire changed very little after the processing time of 7 h. Therefore, it was believed that the C-plane sapphire had reached its processing limit when the processing time was 7 h under this experimental
condition. For the A-, M- and R-plane, the roughness change basically tended to be stable after the processing time was between 10 and 12 h. Finally, the minimum surface roughness Ra of the A-, C-, M- and R-plane were 0.471, 0.307, 0.376 and 0.595 nm by the measured data, respectively. The processing quality of the C-plane after 8 h of polishing was far better than the other three crystal planes from Figure 7, which had achieved a non-destructive surface effect. While the other three crystal surface still had some certain processing defects to achieve the ideal non-damage surface quality.

**Figure 7.** The 500X SEM surface topography with 8 h polishing time of the four crystal orientations for the (a) A-plane, (b) C-plane, (c) M-plane and (d) R-plane.
For the C-plane sapphire wafer, the surface roughness value almost reached the minimum and tended to be stable after 7 to 8 h of polishing, from which could be inferred that the C-direction sapphire had reached its processing limit. For the A-, M-, and R-planes, the workpiece surface still had defects such as local pits and micro bumps after 8 h of processing time. As the polishing time continued to extend to 12~14 h, the surface roughness was stable near its minimum value. It could be inferred that the sapphire wafers with the crystal orientations of the A-, M-, and R-plane had reached their processing limits. Therefore, the final optimal surface roughness value can be considered as the best surface quality of sapphire wafers with different crystal orientations under the experimental conditions.

Crystal models of the four crystal orientations for the A-plane, C-plane, M-plane and R-plane were shown as Figure 8. Although the A-plane and C-plane are both parallel to the C axis, they might exhibit different material properties due to their different atomic arrangements. The atomic arrangement of the C-plane and R-plane of sapphire is completely different from the other two crystal planes of A and M. The C-plane is perpendicular to the C axis direction, and the atomic structure of the R-plane appears as a slope structure obliquely intersecting the C axis direction. Therefore, the material properties (such as the elastic modulus, hardness) exhibited by different crystal orientations of sapphire will be significantly different, which corresponds to the results obtained by the nanoindentation experiment.

![Figure 8. Crystal models of the four crystal orientations for the (a) A-plane, (b) C-plane, (c) M-plane and (d) R-plane.](image-url)

The lattice bond energy of adjacent atomic layers is inversely proportional to the crystal plane distance. The larger the distance between adjacent atomic layers, the smaller lattice the bond energy is. With the lower the binding energy, material can be more easily removed. According to the
characteristics of the hexagonal crystal system, the interplanar spacing $d$ between the adjacent atomic layers of the sapphire $A$, $C$, $M$- and $R$-planes can be calculated according to Formula (2):

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2 + k^2 + hk}{3a^2} + \frac{l^2}{c^2}}}$$  \hspace{1cm} (2)

Here, the $A$, $C$, $M$- and $R$-planes (hkl) of sapphire are calculated according to the distance between the (220), (006), (300) and (036) planes [7]. The sapphire lattice parameters were $a = 4.758$ Å, $c = 12.992$ Å at 293 K.

According to Formula (1), the interplanar spacing $d$ between the adjacent crystal planes of the sapphire $A$, $C$, $M$- and $R$-planes was 1.189 Å, 2.166 Å, 1.375 Å, and 1.161 Å, respectively. The calculation results showed that the crystal plane interplanar spacing $d$ between the adjacent atomic layers of different crystal planes decreased in the order of the C-plane, M-plane, A-plane and R-plane. Therefore, the bonding energy increased in the order of the C-plane, M-plane, A-plane, and R-plane for sapphire with different crystal orientations. It was inferred that the material removal rate of sapphire with different crystal orientations should be C-plane > M-plane > A-plane > R-plane.

In summary, the results obtained through theoretical calculations were very consistent with the experimental results of nanoindentation on different crystal orientations of sapphire and the material removal rate of the polishing processing. Moreover, the research results have great guiding significance for the engineering application of sapphire processing with different crystal orientations.

4. Conclusions

1. Nanoindentation experiments were performed on sapphire with different crystal orientations by nanoindentation technology, and the hardness and elastic modulus increased in sequence according to the C-plane, M-plane, A-plane, R-plane.
2. Polishing experiment results on sapphire with different crystal planes showed that the material removal rate of the $A$, $C$, $M$- and $R$-planes were 3.95, 5.93, 4.16, and 2.47 nm/min. The C-plane sapphire could obtain better surface quality in a shorter processing time.
3. The calculation of the adjacent atomic structures of different crystal orientations indicated that the C-plane was the easiest crystal plane to achieve material removal, and the R-plane was the most difficult to process which was consistent with the previous polishing experiment results. Moreover, the research results have great guiding significance for the engineering application of sapphire processing with different crystal planes.

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