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Effect of alkaline slurries on nano machining CaF_2 crystal

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ABSTRACT

The slurry chemical action affects chemical reaction between the wafer and slurry, and self-conditioning performance of the pad in nano machining process. Fixed abrasive polishing, one of important nano machining technologies, was adopted to achieve a nano precision surface quality of CaF_2 crystal. Five kinds of alkaline regulators, triethanolamine, sodium citrate, sodium carbonate, ethylenediamine and sodium phosphate in slurries with pH 10, were screened in nano machining CaF_2 crystal. The effect on material removal rate (MRR), surface topography and surface roughness was investigated in fixed abrasive polishing of CaF_2 crystal. The results indicated that surface quality is getting better with MRR decreasing. The optimal surface quality of CaF_2 crystal with surface roughness Sa 4.13 nm can be obtained by sodium phosphate slurry with MRR 224 nm/min in fixed abrasive polishing of CaF_2 crystal. The nanometer precision surface quality with high material removal was achieved in nano machining CaF_2 crystal.

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Nano machining; fixed abrasive polishing; CaF_2 crystal; alkaline slurries; material removal rate; surface roughness

1. Introduction

Owing to wide range transmission, excellent achromatic and apochromatic of calcium fluoride (CaF_2) crystal, it is applied to optical components such as lens, prism, windows, etc. [1–2]. Especially in the ultraviolet optical system, CaF_2 crystal is the first choice of lens material in lithography system and high energy laser system because of the ability of high transmissivity, laser-induced damaged threshold, uniformity of refractive indices and low birefringence [3]. On account of its applications in optical system, a high surface quality of CaF_2 crystal is urgently needed. Nano machining technology was adopted to achieve nanometer precision surface quality [4].

Fixed abrasive polishing, one of nano machining methods, can achieve a nanometer precision surface quality and nanoscale material removal simultaneously. Compare to free abrasive polishing, the abrasives are embedded in the polishing pad in fixed abrasive polishing process, and there are no abrasive grains in the slurry,

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which avoids random abrasives to scratch of wafer surface and reduces the cost of slurry [5]. Then, surface material removal is uniform, machining process is simple, and the pollution of polishing slurries to environment is little [6]. In nano machining process, the slurry chemical action produces a softened layer on workpiece surface and affects self-conditioning performance of pad [7]. With the passivated abrasives falling off, new sharp-edged abrasives reveal continually. Then the softened layer is wiped off by mechanical action of the abrasives in fixed abrasive polishing process.

The chemical action of chemical mechanical polishing (CMP) is able to generate a metamorphic layer on workpiece surface and react with pad matrix to affect its self-conditioning performance in nano machining process, which is derived from the chemical additives in the slurry, and the chemical additives are mainly divided into alkaline [8–11], acid [12–14], oxidant [15], complexing agent, etc.. With weakly alkaline slurry under a reduced down pressure, not only a high planarization performance and good quality of the processed copper film surface can be attained, but also the copper polishing rate can be stable for at least 12 h [8]. A higher material removal rate (MRR) in lithium niobate CMP using KOH-H_2O_2 (2 wt%)-citric acid (0.06 M) based slurry than KOH based slurry without additives, surface roughness can also be ultimately improved by CMP process [9]. By adding an appropriate amount of triethanolamine, the working life of fixed abrasive pad (FAP) can be prolong, the lapping process of quartz crystal can keep stable, and surface quality can be improved at the same time [10]. The surface of LBO crystal (110) lattice plane will be slightly damaged and surface roughness can reach 1.94 nm, by the abrasive-free slurry pH 10 with ethanediamine in fixed abrasive polishing [11]. Besides, when LBO crystal surface is the specific lattice plane ($\theta = 90°$, $\varphi = 13.8°$), surface roughness can achieve 0.32 nm with MRR 366 nm/min using citric acid as the additive in slurry pH 5 [12]. Ultra-smooth surface of CdZnTe crystal with surface roughness Ra 0.67 nm can be obtained after polishing of 15 minutes by the optimized independent developed slurry pH 2.5 with nitric acid [13]. Surface quality of Ta will get much better after Ta CMP in H_2O_2-based slurries with CH_3COOH or H_3PO_4, because CH_3COOH and H_3PO_4 can be adsorbed on Ta surface and slow down the formation of dense Ta_2O_5 [14]. Chemical effect dominates removal of Cu surface layers in abrasive-free slurry of H_2O_2 and oxalic acid. With the slurry of H_2O_2 and oxalic acid, part of Cu surface is oxidized by H_2O_2 to CuO which seems to be dissolved by the oxalic acid, and the remaining surface complex is discontinuous CuL (L≡OOC-COO) film which can be removed by mechanical polishing [15].

In this work, various regulators were chosen to polish of CaF_2 crystal by the abrasive-free slurry in nano machining process. Five kinds of alkaline regulators, triethanolamine, sodium citrate, sodium carbonate, ethylenediamine and sodium phosphate in slurries with pH 10, were screened in the polishing experiments. The chemical effect on nano machining process was investigated by comparing MRR, surface topography and surface roughness. The formation mechanism of nanometer precision surface and nanoscale material removal mechanism were discussed.

Table 1. Process parameters of fixed abrasive polishing.

Polishing parameter	Parameter settings
Pressure (kPa)	6.7
Slurry pH	10
Pad speed (rpm)	40
Crystal speed (rpm)	38
Slurry flow rate (ml/min)	60

2. Experimental

Calcium fluoride crystal with a dimension of Φ25 mm×5 mm was adopted in the polishing experiments. A hydrophilic FAP with 3–5 μm diamond abrasive is selected as polishing pad, which has a regular intersecting orthogonal channel pattern [16–17]. Abrasive-free slurry mainly contains with deionized water, surfactant OP-10 agent ($C_{34}H_{62}O_{11}$, a nonionic surfactant) and alkaline regulator. Triethanolamine ($C_6H_{15}NO_3$, TEA), sodium citrate ($Na_3C_6H_5O_7$), sodium carbonate (Na_2CO_3), ethylenediamine ($C_2H_8N_2$, EDA) and sodium phosphate (Na_3PO_4) are adopted in the slurry, respectively. The five alkaline regulators are added in until slurry pH value to 10. The polishing process parameters were showed in Table 1.

Material removal rate is defined as the reduction of thickness per unit time, and calculated using Eq. 1.

$$MRR = \frac{\Delta m \times h_0}{M_0 \times t} \times 10^6 \tag{1}$$

Where the unit of *MRR* is in nanometer per minute, Δm is the mass discrepancy of before and after polishing, h_0 is the thickness before polishing, M_0 is the mass of before polishing, and t is the process duration (in minute). The mass of CaF_2 crystal is determined by Sartorius BS224S precision balance. Surface topography of polished surface is observed with XJX-200 metallographic microscope. CSPM4000 Atom Force Microscope (AFM) is used to measure surface roughness and surface micro topography, and AFM traces are taken in an area of 20μm×20μm.

3. Results and discussion

3.1 Surface topography

Figure 1 shows surface topographies of CaF_2 crystal after nano machining process by five kinds of alkaline slurries, which were tested by microscope. Since there are many deep scratches and pits on CaF_2 crystal surface polished in Fig. 1a and 1b, it can be deduce that mechanical removal plays the main role in polishing by TEA and $Na_3C_6H_5O_7$ slurries. There are some traces of corrosion and slight scratches on CaF_2 crystal surface polished in Fig. 1d and 1e. EDA and Na_3PO_4 can react with CaF_2 crystal in slurries, which generates a softened layer in polishing process. EDA and Na_3PO_4 can react with FAP matrix, improving self-conditioning performance of FAP, which is less than that of TEA and $Na_3C_6H_5O_7$ slurries.

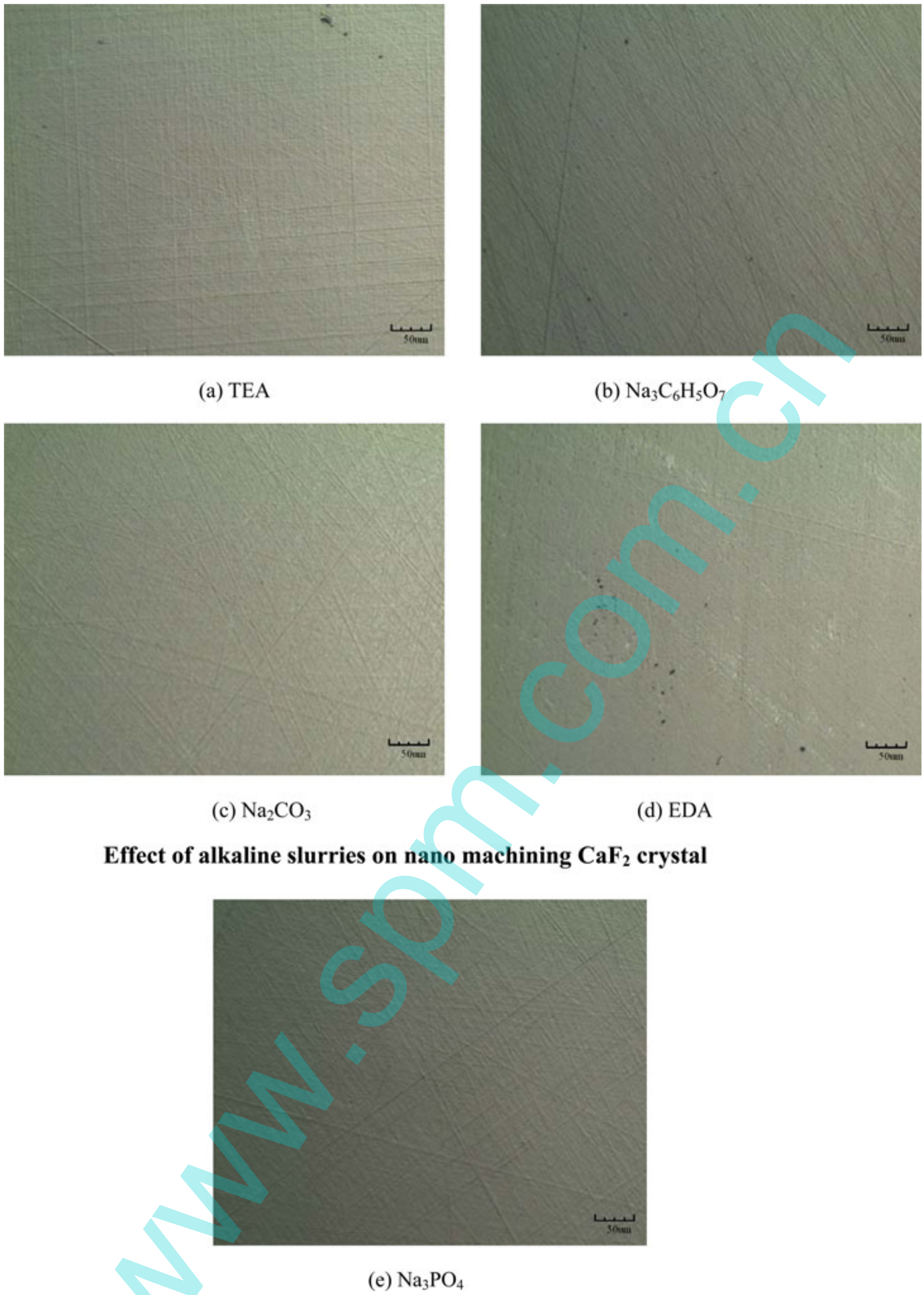

Figure 1. Surface topography of CaF_2 crystal after nano machining.

3.2 Material removal rate

Material removal rate of CaF_2 crystal polished by five kinds of alkaline slurries is illustrated in Fig. 2. The maximum MRR of CaF_2 crystal is 494 nm/min polished by TEA slurry, and the minimum is 224 nm/min by Na_3PO_4 slurry. Figure 3 provides a model of the softened layer removal. The chemical additives in the slurry can react with the crystal, which generates a softened layer on crystal surface. When

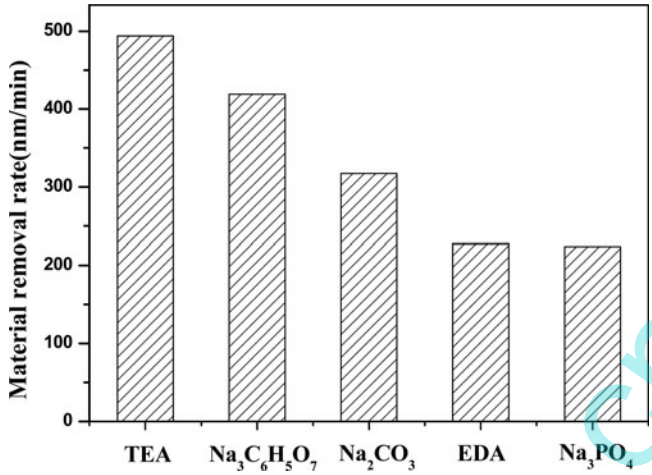

Figure 2. MRR of CaF_2 crystal by five kinds of pH regulators in nano machining process.

relative motion happens between CaF_2 crystal and FAP, the abrasives in FAP scratch soften layer continually to remove. TEA and $Na_3C_6H_5O_7$ as chemical additives almost do not react with CaF_2 crystal, so mechanical removal is the main way. At the same time, TEA and $Na_3C_6H_5O_7$ can react with FAP matrix, which promotes self-conditioning performance of FAP and makes the passivated diamonds fall off and new sharp-edged diamonds reveal fast. Mechanical removal plays the main role, and the abrasives in FAP scratch CaF_2 crystal surface directly. Due to these reasons, MRR of CaF_2 crystal by TEA and $Na_3C_6H_5O_7$ slurries is higher. EDA and Na_3PO_4 can react with CaF_2 crystal as complexing agents of Ca^{2+}, and chemical action between CaF_2 crystal and EDA (or Na_3PO_4) produces a softened layer. The abrasives in FAP scratch the softened layer of CaF_2 crystal, but some reaction products stick on the abrasives. Besides, EDA and Na_3PO_4 react with the matrix of FAP weakly, the new sharp-edged diamond grains reveal slowly. With the passage of time, accumulation of the impurities on the abrasive results in polishing performance degradation of FAP, so MRR of CaF_2 crystal by EDA and Na_3PO_4 slurries decreases in polishing.

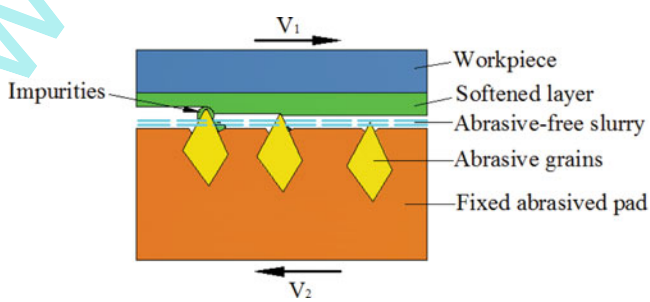

Figure 3. Soften layer removal model.

3.3 Surface roughness

Surface roughness of CaF_2 crystal polished by five kinds of alkaline slurries is revealed in Fig. 4. The optimal surface roughness Sa is 4.13 nm polished by Na_3PO_4 slurry and the worst is 8.31 nm by TEA one. AFM topographies of CaF_2 crystal are compared in Fig. 5. From Fig. 5d and 5e, surface quality of CaF_2 crystal polished by EDA and Na_3PO_4 slurries are better than that of others. EDA is one upstream raw material of ethylene dinitrilotetra-acetic acid (EDTA), and EDTA is a good complexing agent of Ca^{2+}. Na_3PO_4 has excellent complexing ability with Ca^{2+} as a complexing agent, too. The chemical reaction equations are showed in Eq. 2 and Eq. 3, respectively. EDA and Na_3PO_4 can react with FAP matrix at a moderate rate, and the chemical action and mechanical removal work together well. There are some deep scratches on CaF_2 crystal surface by TEA, $Na_3C_6H_5O_7$ and Na_2CO_3 slurries in Fig. 5. TEA as a complexing agent can react with heavy metal ions, but it almost does not react with calcium ions. $Na_3C_6H_5O_7$ and Na_2CO_3 almost do not react with CaF_2 crystal in slurries, too. In addition, TEA and $Na_3C_6H_5O_7$ react with FAP matrix, and the passivated diamonds fall off and the new sharp-edged diamonds reveal fast, which improves self-conditioning performance of FAP. The mechanical removal plays main role with little or no chemical action, so CaF_2 crystal surface polished by TEA, $Na_3C_6H_5O_7$ and Na_2CO_3 slurries performs worse. From Fig. 3, chemical action that occurs between chemical additives and Ca^{2+} can produces a softened layer, and mechanical action of the abrasives in FAP removes the softened layer continually. The surface quality of CaF_2 crystal would be good when the chemical action and mechanical removal work together perfectly.

$$3Ca^{2+} + 2PO_4^{3-} \rightarrow Ca_3(PO_4)_2 \downarrow \quad (2)$$

$$Ca^{2+} + EDA \rightarrow (Ca^{2+} - EDA)\text{clathrate} \quad (3)$$

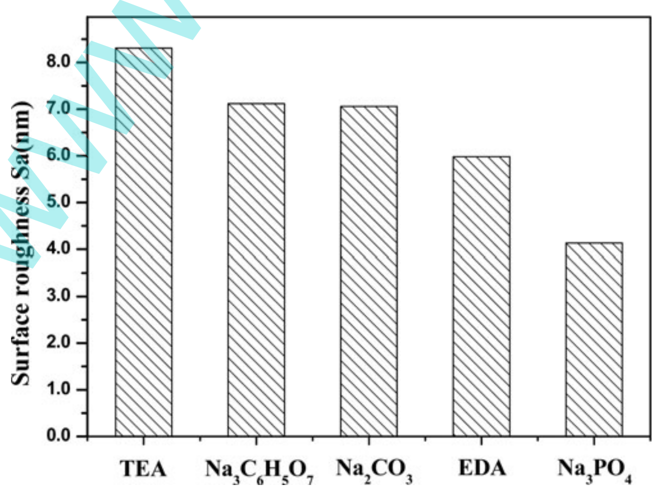

Figure 4. Surface roughness of CaF_2 crystal by five kinds of pH regulators after nano machining.

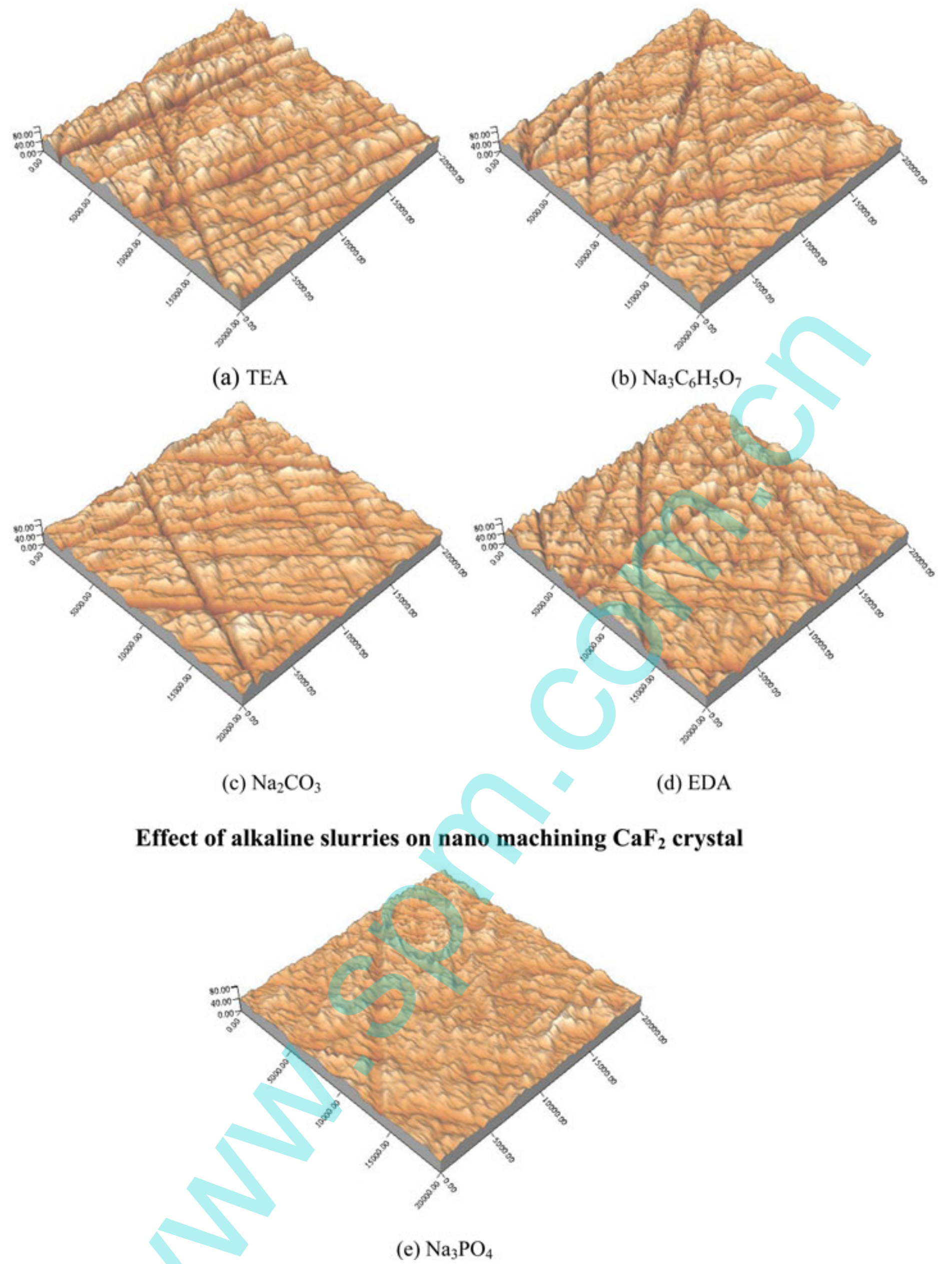

Figure 5. AFM topography of CaF_2 crystal after nano machining.

Material removal rate of CaF_2 crystal polished by TEA slurry is the maximum, while surface quality is the worst in nano machining process. MRR of CaF_2 crystal polished by Na_3PO_4 slurry is the minimum, and surface quality is the best of all. TEA and $Na_3C_6H_5O_7$ can react with FAP matrix intensely, which promotes self-conditioning performance of FAP. EDA and Na_3PO_4 react with FAP matrix weakly, resulting in bad self-conditioning performance of FAP. Surface roughness value of CaF_2 crystal polished is reducing with MRR decreasing. So, among the five alkaline regulators, Na_3PO_4 is the best choice to be added in the slurry in nano machining CaF_2 crystal.

4. Conclusions

The effect of alkaline regulators on nano machining process was investigated in fixed abrasive polishing of CaF_2 crystal. The following conclusions can be drawn.

a. The maximum MRR is 494 nm/min with TEA slurry, and the minimum is 224 nm/min with Na_3PO_4 slurry. The worst surface quality with surface roughness Sa 8.31 nm is in the experiment with TEA slurry, and the best one with surface roughness Sa 4.13 is with Na_3PO_4 slurry.
b. With MRR decreasing, surface quality of CaF_2 crystal is getting better in nano machining process. The optimal surface quality of CaF_2 crystal with surface roughness Sa 4.13 nm can be obtained by sodium phosphate slurry with MRR 224 nm/min in fixed abrasive polishing process.
c. When the appropriate alkaline regulator is added in the slurry of fixed abrasive polishing process, nanometer precision surface quality with high material removal was achieved in nano machining CaF_2 crystal.

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