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Fabrication and plasma resistance properties of transparent YAG ceramics

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Abstract

High quality transparent yttrium aluminum garnet (YAG) ceramics with an average grain size of about 12 μm have been fabricated by a solid state reactive sintering method. Plasma resistance property of the fabricated YAG ceramics was studied and compared with that of the Y_2O_3 ceramics, silicate glass and quartz. The YAG ceramics showed an excellent plasma resistance as well as Y_2O_3 ceramics. After etching in F-plasma for 6 h, the eroded depth of YAG ceramics was about 100 nm. The plasma resistance of YAG ceramics was far better than that of silicate glass and quartz.

Keywords: C. Optical properties; Transparent ceramics; YAG; Microstructure; Plasma resistance

1. Introduction

Plasma dry etching is one of the basic steps used in semiconductor processing for the fabrication of electronic devices [1]. Halogen gas plasma is commonly used for high-speed etching and vertical etching of a wafer. However, high-density corrosive plasma source severely attacks the surface of the components, such as monitor windows, tubes and plates, during the etching process [2]. Conventionally, quartz has been used as the monitor window material in the dry etching chamber, but blurring by plasma attacks has been a serious problem [3]. High-purity aluminum was used as the chamber walls of the plasma etching apparatus. However, aluminum can react with fluorine plasma to thereby produce an Al–F compound. This compound is changed into particles that adversely affect wafer devices [4]. To prevent this, using alumina ceramics or coating an alumina layer on the aluminum walls can significantly reduce the Al–F compound contamination. Nonetheless, the Al–F particles cannot be ignored because of the long-time exposure of the alumina to high-density fluorine plasma. Yttrium aluminum garnet (YAG) and yttrium oxide ceramics have both been recognized as very promising plasma-resistant materials for plasma etching chambers [4,5]. In 2005, Fujita et al. [5] first reported a plasma-resistant member, comprised of Y_2O_3 and/or YAG ceramics, and its fabrication method for a semiconductor manufacturing apparatus, which can significantly reduce the contamination level on a semiconductor wafer. However, the plasma resistance properties of yttrium oxide and/or YAG ceramics were not studied. In 2006, Kobayashi et al. [4] reported a plasma resistant member, which had a base material and a coating layer made of Y_2O_3. At the same time, the plasma resistance properties of Y_2O_3 were studied in their patent. The results showed that the plasma resistance of Y_2O_3 material was much better than that of the conventional Al_2O_3 base material. In 2007, Iwasawa et al. [3] also reported the excellent plasma-resistant properties of Y_2O_3 films prepared by aerosol deposition process on a quartz substrate. However, to the best of our knowledge, the plasma resistance properties of YAG ceramics have not been reported in detail. Furthermore, YAG ceramics have many advantages than

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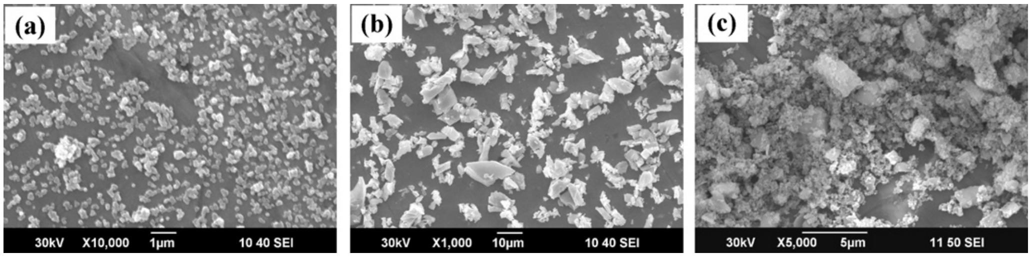

Fig. 1. SEM photographs of starting powders: (a) α-Al_2O_3, (b) Y_2O_3, and (c) powder mixture after ball milling.

Y_2O_3 ceramics for plasma etching chamber or monitor windows, such as low cost, high mechanical strength, easy to fabricate owing to its relatively low melting point than Y_2O_3 and so on.

In the present work, high optical quality transparent YAG ceramics were fabricated by a solid state reactive sintering method. The plasma-resistant properties of different transparent materials such as YAG ceramics, Y_2O_3 ceramics, silicate glass slide and quartz were investigated and evaluated in detail.

2. Experimental procedure

High-purity powders of α-Al_2O_3 (99.99% purity, Shanghai Wusong Chemical Co., Ltd, Shanghai, China), Y_2O_3 (99.999% purity, Yuelong Advanced Material Co., Ltd, Shanghai, China) were used as the starting materials. The starting powders were weighed according to the stoichiometric ratio of YAG, and then mixed by ball milling in ethanol for 12 h, with 0.5 wt.% tetraethyl orthosilicate (TEOS, Sigma–Aldrich, 99.999%) as the sintering additive. The powder mixtures were dried at 120 °C for 24 h in oven and then sieved through 200-mesh screen. After removing organic component by calcining at 800 °C for 3 h, the powders were dry pressed in a stainless steel die at ∼15 MPa. The green body pellets were further cold isostatically pressed (CIPed) at 200 MPa. The compacted pellets were then sintered at 1780 °C for 12 h under 10^{-3} Pa in a vacuum furnace with tungsten meshes as the heating elements. After vacuum sintering, the pellets were further annealed at 1450 °C for 10 h in air. Finally, both surfaces of the as-prepared ceramic samples were mirror-polished by different grade of diamond slurries.

Morphologies of starting powders were observed by a scanning electron microscope (SEM, JSM-6390, JEOM, Tokyo, Japan). The influence of plasma exposure on the surface of the samples was evaluated using a plasma etching machine (Clen100, Advanced System Technology Co., Ltd, England). Four transparent materials were used for the evaluation, including the as-fabricated YAG ceramics, Y_2O_3 ceramics provided by Dr Jin from Shanghai Institute of Ceramics, commercial silicate glass slide and quartz substrate. The samples were placed on the top of the bottom electrode. CF_4 and O_2 were introduced into the reactor. In order to observe the etching rate, one half of each sample was covered with a silicate glass slide to avoid plasma etching. The plasma exposure time was up to 6 h and details of the test conditions are listed in Table 1. After plasma exposure, the optical transmittances of all the samples were measured by a UV-VIS-NIR spectrometer (Carry 5000 Spectrophotometer, Varian, USA). The eroded surfaces were observed by a scanning electron microscope (SEM, JSM-6360A, JEOM, Tokyo, Japan) equipped with EDS. The erosion depths were analyzed using a surface profiler (Alpha-step IQ, KLA-Tencor, USA).

3. Results and discussion

Fig. 1 shows SEM morphologies of the starting powders before and after ball milling. The α-Al_2O_3 powders were uniform with a narrow particle size distribution and fairly well-dispersed. The average particle size of the α-Al_2O_3 powder was about 300 nm in diameter. The Y_2O_3 powders were relatively wide distribution from submicron to micron-scale and the mean particle size was about 4 μm, which were agglomerated with each other. The large particles of Y_2O_3 and the fine particles of α-Al_2O_3 were homogeneously mixed by ball milling (shown in Fig. 1(c)).

Fig. 2 shows the mirror-polished YAG ceramic samples as-fabricated. The thickness of all samples was polished to 1 mm. From the figure, it can be seen that high quality transparent YAG ceramics have been successfully fabricated and read-through letters were clearly resolved. Obviously, the as-fabricated

Table 1
Plasma etching conditions.

Parameters	Condition
RF power, W	200
Bias voltage, V	311
Chamber pressure, mTorr	30
Process pressure, mTorr	∼418
CF_4, sccm	40
O_2, sccm	10

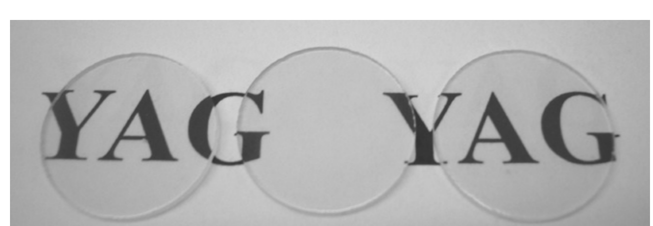

Fig. 2. Photo of the as-prepared transparent YAG ceramics.

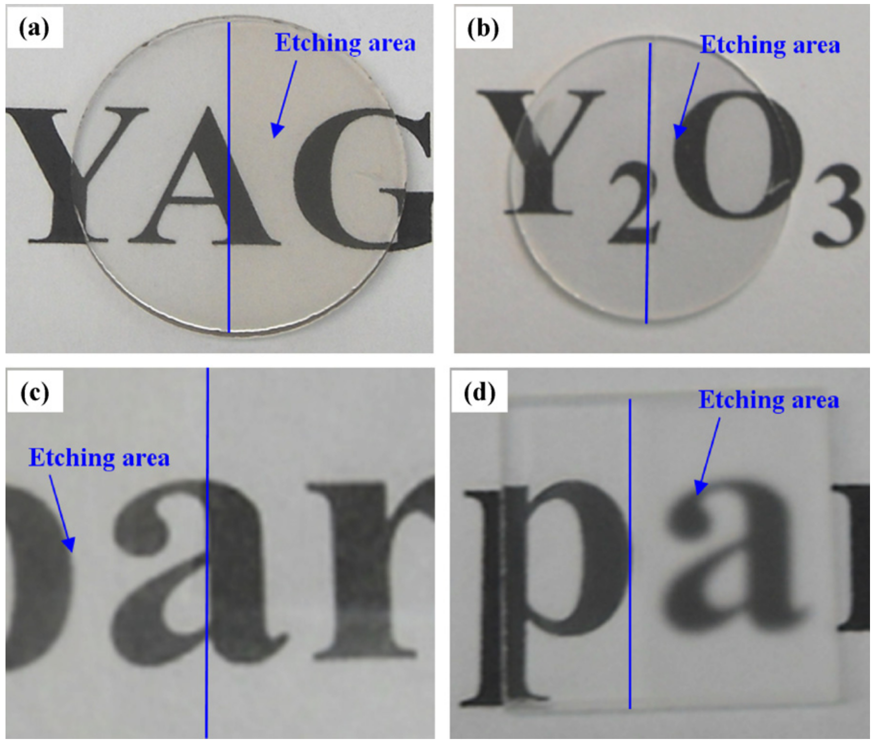

Fig. 3. Photos of four transparent materials after plasma etching for 6 h: (a) YAG ceramics, (b) Y_2O_3 ceramics, (c) silicate glass slide and (d) quartz.

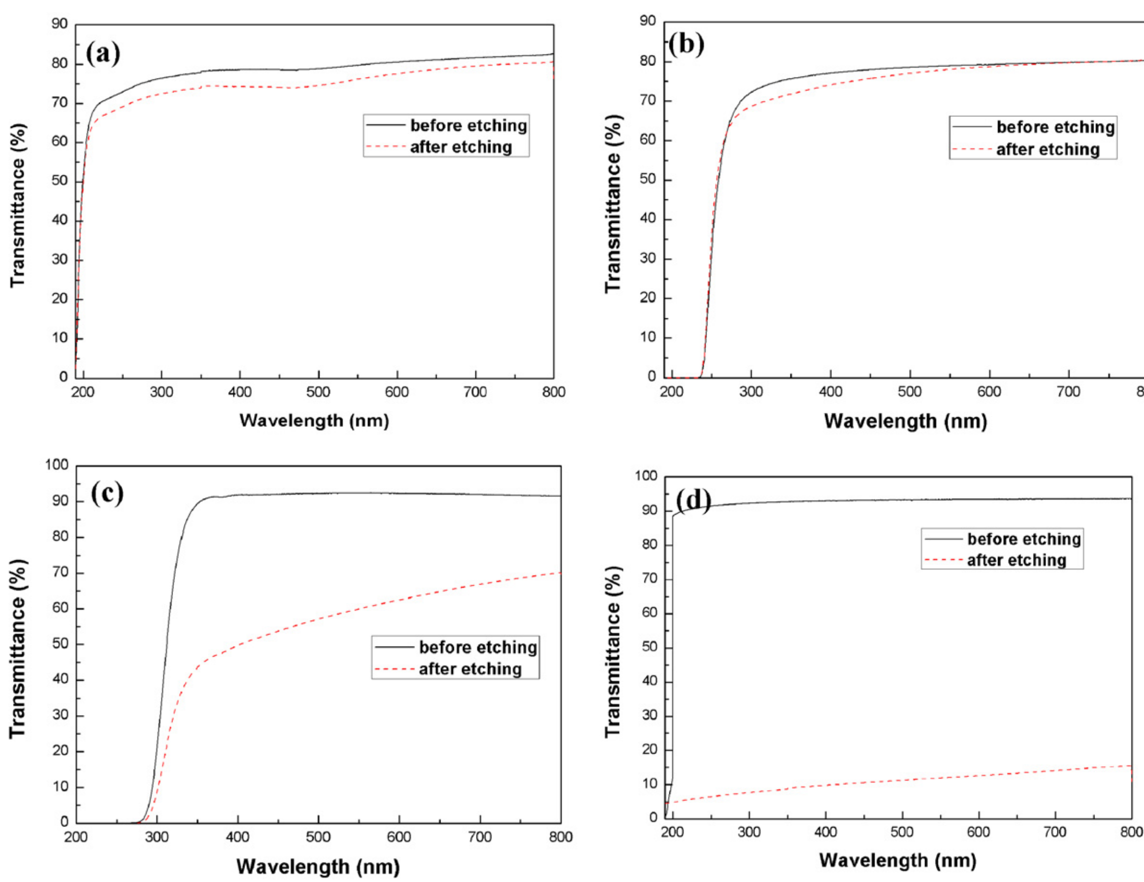

Fig. 4. Transmittances of samples before and after plasma etching for 6 h: (a) YAG ceramics, (b) Y_2O_3 ceramics, (c) silicate glass and (d) quartz.

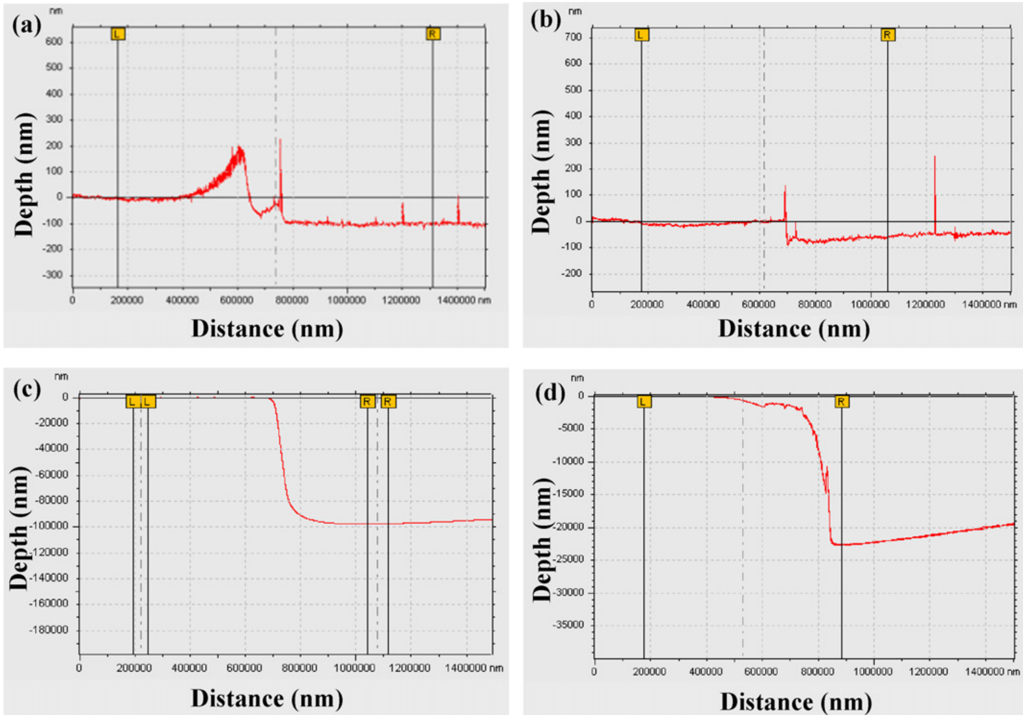

Fig. 5. The eroded depth of four samples after plasma etching for 6 h: (a) YAG ceramics, (b) Y_2O_3 ceramics, (c) silicate glass and (d) quartz.

transparent ceramics can be used as monitor windows for the plasma etching apparatus.

To evaluate the plasma resistance of as-fabricated YAG ceramics more clearly, other transparent materials including Y_2O_3 ceramics, commercial silicate glass slide and quartz substrate were selected and etched at exactly the same conditions as for YAG ceramics. Fig. 3 shows the photos of four transparent materials after plasma etched for 6 h. One half of each sample was covered by a silicate glass slide and the other half was exposed to plasma erosion directly. As can be seen from the figure, YAG and Y_2O_3 ceramics were still transparent after plasma treatment, however the silicate glass slide and quartz substrate became translucent after etching.

In order to compare the transparency, in-line transmittances of each sample before and after plasma etching were measured. Fig. 4 shows the plasma resistance in terms of the optical properties for each transparent material. For YAG and Y_2O_3 ceramics, the decrease of transmittance was less than 5% in the visible region after etched for 6 h. For silicate glass slide and quartz, drastic decrease of transmittance was observed in the same region, which decreased by more than 30% and 80%, respectively. It means that the sample surfaces have been heavily attacked by the plasma.

Fig. 5 shows the eroded depth of four samples after plasma exposure in CF_4/O_2 for 6 h, which is measured by the surface profile. For YAG and Y_2O_3 ceramics, the eroded depth was about 100 nm and 60 nm, respectively. However, the eroded depth of silicate glass slide and quartz was about 97,000 nm and 22,000 nm, respectively. Clearly, both the two transparent ceramics have excellent plasma resistance properties. Silicate glass had the worst plasma resistance among all of the four materials.

Fig. 6 shows SEM micrographs of the surfaces of the samples before and after plasma etching. Fig. 6(a) shows the surface of as-fabricated YAG ceramics before plasma etching. The average grain size of the YAG ceramics was about 12 μm and there were almost no pores and impurities in or between the grains, indicating the high density of the transparent ceramics. Some small etching pits can be found on the surface of YAG ceramics (shown in Fig. 6(b)). Similarly, there were only a few etching pits on the surface of Y_2O_3 ceramics (shown in Fig. 6(d)). The chemical composition of the erosion zone of YAG and Y_2O_3 ceramics was analyzed by EDS. No other elements were found at the erosion zone and they were still the original chemical compositions of two kinds of ceramics (1# and 2# in Fig. 7). Fig. 6(e) and (f) shows the microstructures of silicate glass before and after plasma treatment. Obviously, silicate glass was severely damaged after etching for 6 h. The surface of glass became coarse and rough, which was the cause of transmittance drop (shown in Fig. 4(c)). EDS analysis for silicate glass slide shows that the chemical composition of the sample was changed after etching (3# and 4# in Fig. 7). F element remained on the surface of glass after exposure in CF_4/O_2 plasma. This indicates that F-plasma heavily reacts with silicate glass to form F contained glass. Fig. 6(g) and (h) shows the microstructure of quartz substrate before and after plasma etching. The etched surface of quartz was different from that of silicate glass. This implied a different etching mechanism of two kinds of materials. EDS results showed no difference of the chemical composition before and after erosion (5# in Fig. 7). During plasma etching, F plasma may react with SiO_2 to form

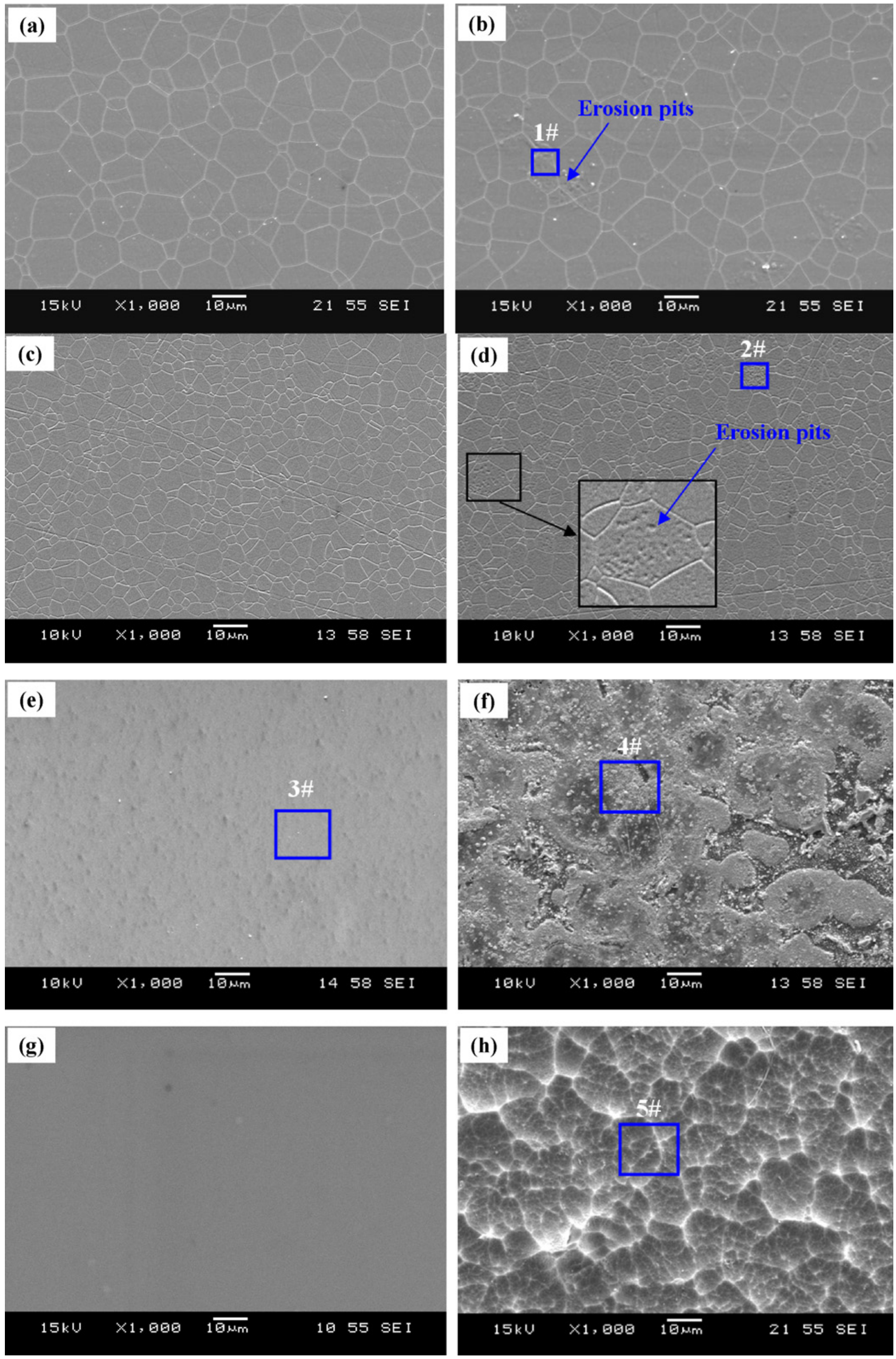

Fig. 6. Micrographs of four transparent materials before (left) and after (right) plasma etching: YAG (a and b), Y_2O_3 (c and d), silicate glass (e and f), quartz (g and h).

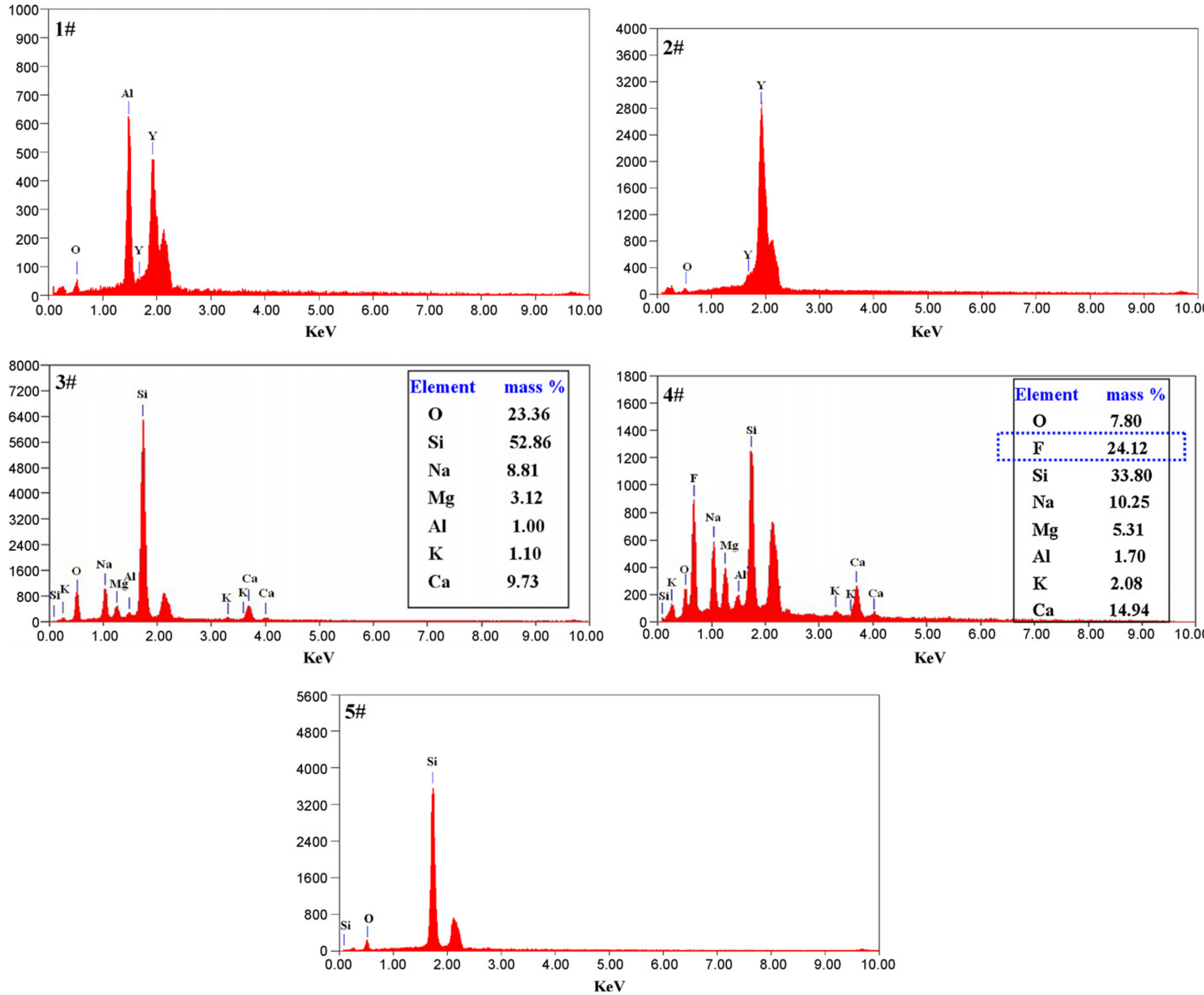

Fig. 7. EDS patterns of four transparent samples: 1#, 2#, 3#, 4# and 5# marked in Fig. 6, respectively.

SiF_4, which is in the form of gaseous at room temperature [1,6]. Therefore, F plasma can erode the quartz severely without any particles remained on the surface of quartz.

4. Conclusions

High optical quality transparent YAG ceramics were fabricated via a solid state reactive sintering method under vacuum. The average grain size of the YAG ceramics was about 12 μm and there were almost no pores and impurities existed in or between the grains. The YAG ceramics as well as Y_2O_3 ceramics shows excellent plasma resistance properties. After etching in F plasma for 6 h, the eroded depth of YAG ceramics was about 100 nm. On the contrary, plasma resistance of the silicate glass and quartz was very weak and the eroded depth of them reached as high as 97,000 nm and 22,000 nm, respectively. The YAG ceramics obtained may have potential use as monitor windows of plasma etching apparatus because of its higher strength and lower cost than those of Y_2O_3 ceramics.

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