Spectroscopic characterization of fluorine atoms in atmospheric pressure He/SF_6 plasmas

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We investigate reactive fluorine atom spectroscopic characterization in atmospheric pressure of He/SF_6 plasma using atomic emission spectrometry. As input radio frequency (RF) power levels are raised from 140 to 220 W, the emission spectra of 685.60 (3p4D→3s4P transition) and 739.87 nm (3p4P→3s4P transition) increase significantly. Moreover, an optimal value of SF_6 volume concentration in the production of fluorine radicals, which is 0.8% is achieved. Addition of certain amounts of O_2 into He/SF_6 plasma results in the promotion of SF_6 dissociation. Emission intensities of fluorine atoms show the maximum at the O_2/SF_6 ratio of 0.4.

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The manufacture of damage-free optics for advanced optical systems within an acceptable period of time and cost has been providing unique challenges in manufacturing. Conventional methods of optical finishing relied mostly on plastic deformation and brittle fracture to cut away material from the workpiece. These inevitably involved physical force at the micro scale and created damage in the subsurface of the material being treated. Subsurface damage can greatly influence performance of the manufactured optical component[1,2].

Atmospheric pressure plasma polishing (APPP) is a novel optical manufacturing technology. Relying upon chemical reaction between work surface atom and neutral radical generated by the plasma, APPP transforms surface material into a volatile byproduct. There is no mechanical contact with the surface, avoiding subsurface damage[3,4]. Plasma chemical vaporization machining (PCVM) was developed by Osaka University, and their research work was mainly focused on the processing of silicon-on-insulator (SOI) wafer and improving the thickness uniformity of quartz crystal wafer[1,5]. Reactive atom plasma (RAP) process was developed by RAPT^{TM} Industries. Cranfield University has been using the RAP process to etch ultra low expansion (ULE) glass[2,6]. The intensity of reactive atoms as an important plasma parameter for controlling the removal rate and its efficiency should be investigated. The spectroscopic methods are frequently favored in diagnosing the atmospheric pressure plasma characteristics[7].

In the present work, a self-designed plasma discharge device is utilized to investigate the properties of atmospheric pressure plasma using He and SF_6 mixture. The characterization of active fluorine atoms is studied by atomic emission spectrum. The dependence of plasma emission intensity of active fluorine atoms on the applied radio frequency (RF) power and the SF_6 volume concentration is presented. In addition, the effect of adding O_2 into He/SF_6 plasma on the dissociation of SF_6 molecules and emission intensity of active fluorine atoms are investigated.

The experimental setup is illustrated in Fig. 1. The needle electrode made of stainless steel with outside diameter of 1 mm was placed inside a quartz tube, which was surrounded by a poly tetra fluoro ethylene (PTFE) cover to supply process gas to the electrode. The plasma-generating unit consists of a needle electrode connected to the RF source and an XY table connected to the ground. The fused quartz workpiece acts as a dielectric material covering on the ground electrode to constitute the dielectric barrier discharge (DBD). A stable plasma is generated in the narrow gap between the electrode and the fused quartz by applying a capacitively coupled RF field by means of a 13.56-MHz RF generator connected through an impedance matching box. Flow rates of the gases were precisely monitored by independent leak valves connected to gas cylinders in series with linear mass flow meters. The optical emission of the plasma column is transmitted through an optical fiber located 5 cm from the tip of the needle and recorded by a spectrometer (AvaSpec-2048, Avantes Inc, Netherlands). The spectrometer, whose applications range from 200 to 1100 nm, has a fiber optic entrance connector with a 50-μm slit .

The typical spectrum of the He/SF_6 plasma is shown in Fig. 2. Most lines are identified as neutral He and F lines. Dissociation of SF_6 is confirmed by numerous lines. Figure 3(a) shows the change trend of the emission intensity of reactive fluorine atoms when the

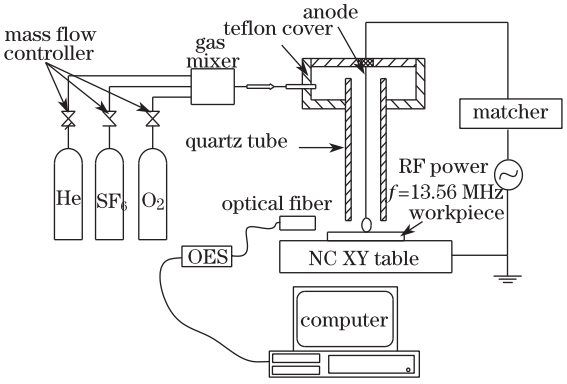

Fig. 1. Schematic diagram of the APPP system.

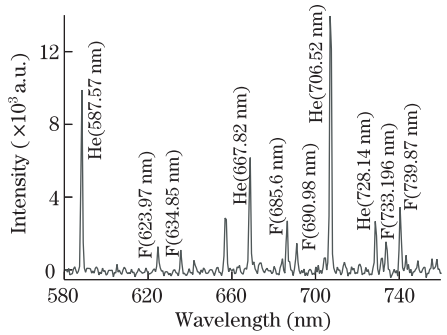

Fig. 2. Typical spectrum of the He/SF_6 plasma.

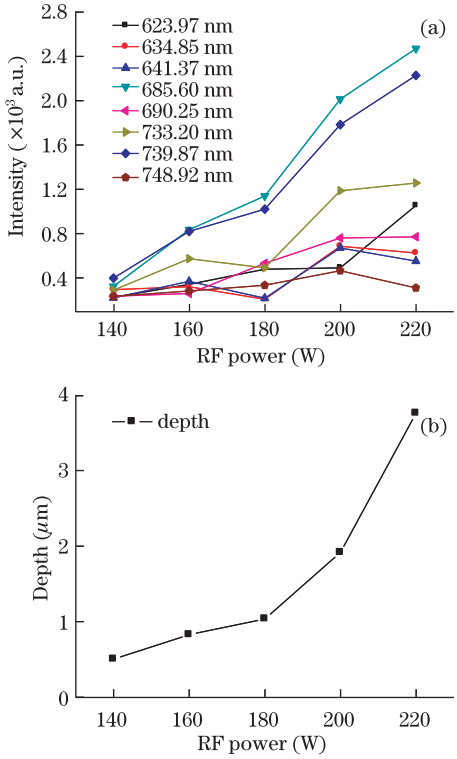

Fig. 3. (a) Emission intensity of reactive fluorine atoms, and (b) depth of removal footprint at various RF power supplies.

operating RF power supply varies from 140 to 220 W at an increasing step of 20 W. In atmospheric pressure He/SF_6 plasma, eight spectra show the emission of atomic fluorine at different wavelengths. With increasing applied RF power, the increased intensity of emission spectrum range differs. A few changes are not obvious, except the maximum emission intensity of the two emitted lights which are λ=685.60 (3p4D→3s4P transition) and 739.87 nm (3p4P→3s4P transition). The consistency increased noticeably[8,9].

Figure 3(b) exhibits the depth of the footprint with the same electrode scanning dwelling time but with different RF powers. The removal rate is higher as the emission intensity of the reactive fluorine atoms increases. A gas containing fluorine is generally used as reactive gas to remove silicon dioxide components and He is used as plasma gas. Figure 4 shows the curve of the emission intensity of different reactive fluorine atoms at various SF_6/He flow ratios. The process conditions are 220 W RF power, 1.5 L/min He flow, and SF_6 volume concentration

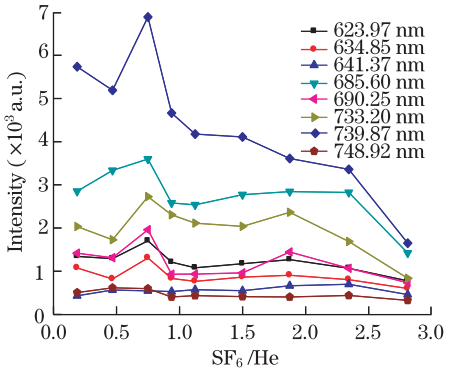

Fig. 4. Curves of the emission intensity of different reactive fluorine atoms at various SF_6/He ratios.

from 0.2% to 3%. It is evident from the figure that the emission intensity of reactive atoms increases with SF_6 concentration when it is less than 0.8%. When increased with the addition of more SF_6 molecules, electron density decays due to the process of electron attachment to SF_6 molecules. This impacts on the dissociation of SF_6 molecules. The emission intensity result coincides with the measurement result on removal rate. The smaller gas ratio is suggested to be conducive to the etching rate increase and the optimum volume concentration of SF_6 in the system is approximately 0.8%[10].

A gas containing fluorine is generally used for plasma etching to move silicon dioxide components. The removal process is performed by chemical reactions. Adding the appropriate auxiliary gas O_2 in the reactive gas SF_6 can move the reaction to the etching direction and improve removal efficiency[5]. Figure 5 shows the relationship between the O_2/SF_6 ratio and removal depth of fused quartz with the electrode at rest. The supplied power, gap distance, dwelling time, and flow rates of He and SF_6 were fixed at 200 W, 1.5 mm, 1 min, 1.2, and 0.04 L/min, respectively. The flow rate of O_2 varied from 0 to 24 mL/min. The shape of the unit removal profile was measured by the Stylus Profiler. The shape follows the Gaussian curve, and the rotation is symmetrical. The width of removal profile is almost unchanged. Consequently, the removal depth was used to measure the removal rate. The O_2/SF_6 ratio of 0.4 shows the maximum removal rate.

Figure 6 shows the optical emission spectrum of the plasma generated at various O_2/SF_6 ratios. The

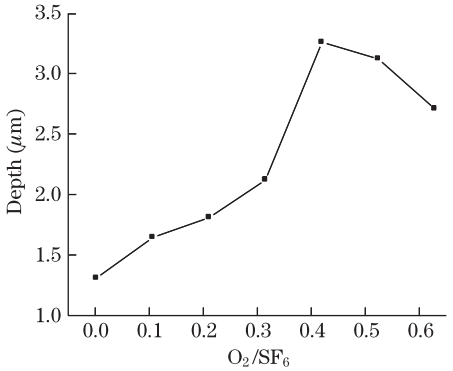

Fig. 5. Relationship between O_2/SF_6 ratio and removal depth of fused quartz.

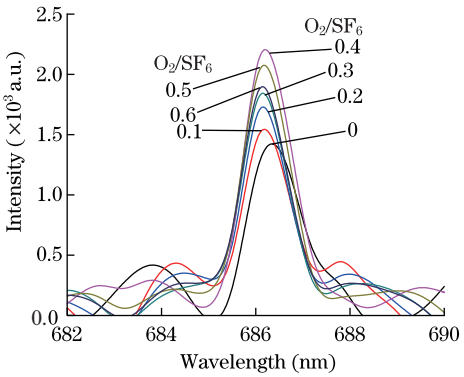

Fig. 6. Optical emission spectra of O_2/SF_6/He plasma.

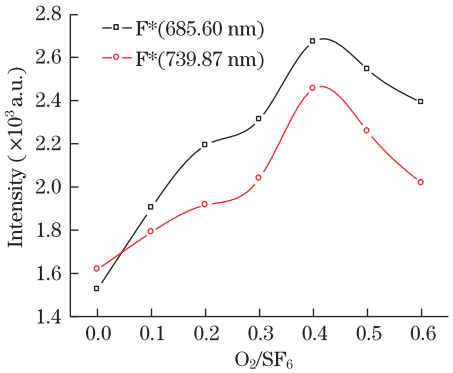

Fig. 7. Dependence of relative emission intensities from F atom (λ= 685.60 and 739.87 nm) on the O_2/SF_6 ratio.

tendency of emission intensity on the two emitted lights from fluorine atom (λ=685.60 and 739.87 nm) is shown in Fig. 7.

The two curves follow the coincident variation tendency and reach their maximum at the identical concentration ratio of 0.4, where most fluorine radicals are produced. By adding an appropriate amount of oxygen, the removal rate seems to increase as a result of the increase in the number of fluorine atoms. Fluorine atoms are dominant reactive species in the dry etching of fused quartz. Additional oxygen gas promotes the dissociation of SF_6 molecules, and the peak value was obtained at the O_2/SF_6 ratio of 0.4.

In conclusion, atmospheric pressure He/SF_6 plasmas are produced and the spectroscopic properties of reactive fluorine atoms are investigated using optical emission diagnostics. When the input RF power level increases from 140 to 220 W, the emission spectra of 685.60 and 739.87 nm significantly increase due to increase in the energy of electrons which facilitates increase in collisions between particles. When the SF_6 volume concentration varies from 0.2% to 3%, the optimal value of dissociation of SF_6 molecules is 0.8%. This suggests that with excessive SF_6 molecules participating in the discharge process, the electron density decays because of the process of electron attachment to SF_6 molecules. This in turn impacts on the dissociation of SF_6 molecules. To investigate the effects of O_2 on the dissociation of SF_6 molecules, the optimal oxygen concentration for production of fluorine radical is determined by means of optical actinometry. The results indicate that additional oxygen gas can promote the dissociation of SF_6 molecules, and the peak value is obtained at $O_2/SF_6 = 0.4$.

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