Research on the chemical reaction in CF_4 plasma during fused silica processing

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Abstract. The chemical reaction involved in the processing of Atmospheric Pressure Plasma Jet (APPJ) produced from CF_4 precursor has been explored. The gas-phase reaction in CF_4 plasma and chemical reaction on SiO_2 surface, which are the two crucial stages in plasma processing were investigated. The roles of gas-phase excited species, especially F atoms and CF_2 molecules, were examined as they contribute to substrate etching and fluorocarbon film formation. Moreover, the relative concentrations of excited state species of F atoms and CF_2 were acquired for CF_4 plasma. The densities of F atoms increased dramatically with increasing applied RF power, whereas CF_2 molecules decreased monotonically over the same power range. The spectrum of the F atoms and CF_2 molecules fallowed the same tendency with the increasing concentration of gas CF_4, and then the emission intensity of reactive atoms decreased with more CF_4 molecules participating. Addition certain amount O_2 into CF_4 plasma resulted in promoting CF_4 dissociation, O_2 can easily react with the dissociation product of CF_2 molecules, which inhibit the compound of the F atoms, and with the increasing concentration of O_2.

Introduction

Atmospheric Pressure Plasma Jet (APPJ) as a novel optical manufacturing technology has been developed in recent years[1]. It is based on pure chemical reaction between silicon-based materials surface atom and reactive fluorine radicals generated by the plasma, then the volatile product SiF_4 is generated to remove the material at atmospheric pressure, which avoids any introduction of damage to the processed surface. Thereby, the APPJ is a very promising and powerful technique that can be employed in the rapid damage-free optical manufacturing[2-3].

Various kinds of physical and chemical steps are involved during APPJ processing, which mainly includes three reaction systems: plasma excitation, the ionization of reaction gases and the reaction between plasma and the workpiece surface[4]. Fluorocarbon plasmas have been widely used in the etching of SiO_2 substrates, and the number of SiO_2 etching processes is increasing in manufacturing. A number of plasma models have been reported for CF_4, however, some models focus exclusively on gas reactions and do not include etching or surface reactions, while others include simple and detailed treatments of surface reactions. Owing to the complex gas and surface chemistry in fluorocarbon plasma etching of SiO_2, which includes a number of reactive atoms and molecules, experiments are often required to be coupled with a numerical analysis to gain a better understanding of the fundamental processes underlying the etching. Thus, it is important for SiO_2 etching in CF_4 plasma that the chemical reaction incorporates gas-phase reaction as well as surface chemical reaction.

In this paper, the chemical reaction for CF_4 plasma etching of SiO_2 is presented, taking into gas-phase reaction and surface chemical reaction. The optical emission spectroscopy (OES) is acquired and analyzed by atomic emission spectroscopy technology, the dependence of relative concentrations of F atoms and CF_2 molecules on the plasma parameters is investigated, and the affection of plasma parameters in CF_4 plasma systems on etching and polymerizing behavior is established.

Surface chemical reactions in CF_4 plasma

Plasma etching involves various kinds of physical and chemical steps, F atoms generated in the plasma diffused to the substrate surfaces, and the species adsorbed on the substrates react with the SiO_2 molecules to form etch products, which then desorb and diffuse back into the plasma. In general, the gas-phase reaction in CF_4 plasma and chemical reaction on SiO_2 surface are the two crucial stage in plasma processing.

In gas-phase reaction, F atoms are produced mainly through electron-impact dissociation of the feedstock CF_4, and its fragments fluorocarbon radicals CF_x(x=1-3) also is ionized simultaneity, the fluorocarbon radicals CF_x(x=1-3) are then further dissociated into smaller radicals also by electron impact. Moreover, the fluorocarbon radicals CF_x(x=1-3) recombine with F atoms to form CF_{x+1}. The equations of F atoms dissociation and recombination are written as

$$CF_4 + e \rightarrow CF_3 + F + e \tag{1}$$

$$CF_3 + e \rightarrow CF_2 + F + e \tag{2}$$

$$CF_x(x=1-3) + F \rightarrow CF_{x+1} \tag{3}$$

According to the CF_4 plasma gas-phase reaction process, it can be seen that the CF_4 molecular dissociated F atoms and fluorocarbon radicals by electronic collision, and at the same time, the recombination reaction between excitation atom and ionization products also happened. Three mainly types of ionization products of CF_4 are fluorine atom, fluorocarbon radicals and fluorocarbon ion.

CF_4 plasma generated such as active atoms, ions and free radicals occurred various physical and chemical reactions with the SiO_2 surface, surface reaction process can be divided into three steps: (1) the adsorption of reactant molecules and free radicals in the solid surface; (2) the adsorption of reactant molecules and free radicals and solid surface reaction, adsorption product molecules generated on the solid surface; (3) the product molecules adsorbed on the solid surface desorption, and through diffusion away from the solid surface.

The removal of surface atoms of SiO_2 substrates is attributed mainly to reactions through simultaneous exposure of reactive F atoms, the neutral atoms and molecules adsorbed react with the SiO_2 surfaces to form surface reaction layers. The fluorine atoms, fluorocarbon radicals and polymers are bonded to SiO_2 surface sites, gradually forming SiF_x (x=1-4) and etching of fully fluorinated Si sites SiF_4 and then diffusion away from the surface.

During CF_4 plasma dicharge, the F atoms and CF_x(x=1-3) molecules are generated by high energy ion bombardment, the ionization thresholds of CF is 18eV, while the thresholds of CF_2 is low at 14eV. As the lower efficient collision for excitation, CF_2 is the most abundant molecular radical species present in CF_x(x=1-3) molecules. The gas-phase CF_2 concentration is high, causing the slow gas-phase concatenation reactions to occur. These processes produce high-mass neutrals and ions, which are the real polymer precursors. Thus, the CF_2 plays a significant role in surface polymerization. For these reasons, it is necessary to investigate the density of F atoms and CF_2 molecules in CF_4 plasma processing with the experimental parameters.

Atomic emission spectroscopy of F and CF_2

The excitation and ionization of CF_4 directly influence the concentration of charged species, which plays a sinificant role in chemical reaction processing. It is demonstrated that by changing the experimental conditions, e.g. input power, flow rate of CF_4 and gas feed composition, it is possible to change the concentration of F atoms and of CF_2 molecules as well as the extent of ion bombardment, and therefore the etching and polymerizing behaviour of the discharge.

The influences on F atoms and CF_2 molecules spectra by the key factors of CF_4 plasma including input power, flow rate of CF_4 and gas feed composition are studied using single factor method. Input power is the provider of energy for the whole system, so it plays a significant role in the CF_4 plasma discharge. When the input power exceeds the critical discharge thresholds, the stable glow plasma discharge is generated. However, with the input power increased, the situation of plasma discharge will be transformed into the arc discharge, which produces instantaneous high temperature will greatly influence the plasma processing. Thus, the range of input power should ensure the stability of plasma discharge.

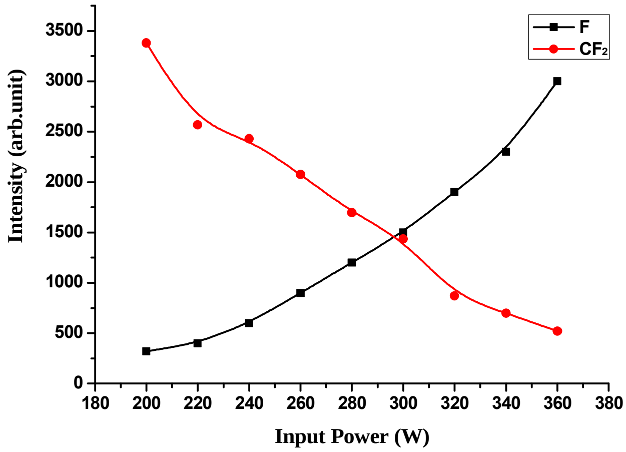

Figure 1. Emission intensity for F atoms and CF_2 molecules with input power

According the experimental results, in a CF_4 plasma, relative CF_2 molecules concentrations decrease with increasing input power, In turn, F atoms spectra is proportional to the power. it suggesting that the collision movement of ionization electron in plasma is more intense with input power increasing, the subsequent electron impact decomposition of plasma species after precursor fragmentation, more F atoms is created by electron impact dissociation of CF_2 molecules,

CF_4 is the provider of F atoms and CF_2 molecules, so the flow rate of CF_4 may affect the plasma spectra greatly. As shown in Fig.2, the emission intensity for F atoms and CF_2 molecules as a function of CF_4. The change trends of F atoms and CF_2 molecules are basically the same, and the spectrum intensity of F atoms is far greater than the intensity of CF_2 molecules.

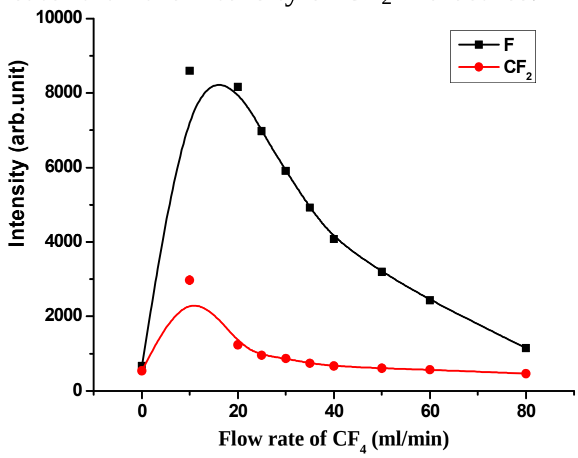

Figure 2. Emission intensity for F and CF_2 species as the flow rate of CF_4

From the spectra curve, it can be seen that the influence on F atoms is more obvious than CF_2 molecules under the condition of constant input power. The emission intensity firstly rises with the increase of CF_4 and then reach a peak value at about 20 ml/min, when the flow of rate of CF_4 exceeds 20 ml/min, both of the emission intensity decrease. However, the emission amplitude of F atoms decreases obviously, and the intensity of CF_2 molecules remain unchanged. The intensity of F atoms which actived by input power reaches the maximum value at 20 ml/min, when the flow rate of CF_4 increased, the mumber of F atoms in the ground state is greater than the mumber of excited states, which causes the emission intensity decreased.

In the CF_4 plasma processing, O_2 as the auxiliary gas is mixed into CF_4 to increase the intensity of the reactive F atoms and hence speed up the material removal rate. To investigate the effects of O_2 on the plasma spectra, by changing the ratio of O_2 to CF_4 while keeping other parameters unchanged, the emission intensity for F and CF_2 species as a function of O_2/ CF_4 as Fig. 3.

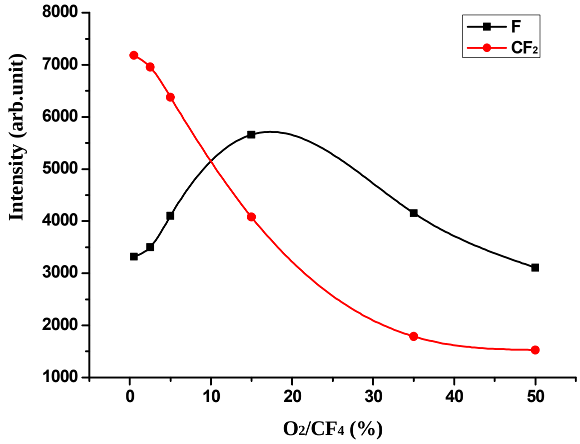

Figure 3.Emission intensity for F and CF_2 species as a function of O_2/ CF_4

As can be seen in Fig. 3, the emission intensity of F atoms rises with the O_2 addition, and then reach a peak value at about 20% of O_2/ CF_4. It is possible that the intermediate products CFx(x=1-3) ionized from CF_4 can easily react with O_2 to produce COF_2, CO or CO_2. This process will prevent the active particles in plasma from recombination, and then, more active F atoms are released out. Meanwhile, the CF_2 and O combine prior to desorbing from the surface as CF_2O, thereby reducing the amount of scattered CF_2. Howerver, when the O_2 ratio continues increased, the recombination process between O_2 and CFx reach adsorption saturation, the excess O_2 will not maintain the activity of F atoms. Thus, the emission intensity of F atoms decreased with high ratio of O_2/ CF_4. And the emission intensities of F atoms raised and reached the maximum at the O_2/CF_4 ratio of 20%.

Conclusions

The chemical reaction involved in the CF_4 plasma was investigated, the two crucial stages of gas-phase reaction in CF_4 plasma and chemical reaction on SiO_2 surface were investigated to reveal the formation mechanism of the surface during APPJ. F atoms and CF_2 molecules were the excited species that contribute to substrate etching and fluorocarbon film formation. Emission spectroscopy technology was employed to analyze the functions of F atoms and CF_2 groups ionized from reaction gas CF_4. The effects of different atmospheric plasma processing parameters on the ionization of reaction gas CF_4 are studied. The CF_2 molecules concentrations decreased with increasing input power, while the spectra F atom was proportional to the power. The change trends of F atoms and CF_2 molecules are basically the same with the increase of CF_4, and the spectrum intensity of F atoms is far greater than the intensity of CF_2 molecules. Addition O_2 into CF_4 plasma prevented the F atoms from recombination with CF_2 molecules, moreover, the CF_2 molecules reacted with O_2 and produced COF_2, CO or CO_2, and reached the maximum at the O_2/CF_4 ratio of 20%.

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