Research on the chemical reaction in CF₄ 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 CF₄ precursor has been explored. The gas-phase reaction in CF₄ plasma and chemical reaction on SiO₂ surface, which are the two crucial stages in plasma processing were investigated. The roles of gas-phase excited species, especially F atoms and CF₂ 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 CF₂ were acquired for CF₄ plasma. The densities of F atoms increased dramatically with increasing applied RF power, whereas CF₂ molecules decreased monotonically over the same power range. The spectrum of the F atoms and CF₂ molecules fallowed the same tendency with the increasing concentration of gas CF₄, and then the emission intensity of reactive atoms decreased with more CF₄ molecules participating. Addition certain amount O₂ into CF₄ plasma resulted in promoting CF₄ dissociation, O₂ can easily react with the dissociation product of CF₂ molecules, which inhibit the compound of the F atoms, and with the increasing concentration of O₂.

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 SiF₄ 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 SiO₂ substrates, and the number of SiO₂ etching processes is increasing in manufacturing. A number of plasma models have been reported for CF₄, 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 SiO₂, 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 SiO₂ etching in CF₄ plasma that the chemical reaction incorporates gas-phase reaction as well as surface chemical reaction.

In this paper, the chemical reaction for CF₄ plasma etching of SiO₂ 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 CF₂ molecules on the plasma parameters is investigated, and the affection of plasma parameters in CF₄ plasma systems on etching and polymerizing behavior is established.
Surface chemical reactions in CF₄ 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 SiO₂ molecules to form etch products, which then desorb and diffuse back into the plasma. In general, the gas-phase reaction in CF₄ plasma and chemical reaction on SiO₂ 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 CF₄, and its fragments fluorocarbon radicals CFₓ (x=1-3) also is ionized simultaneously, the fluorocarbon radicals CFₓ (x=1-3) are then further dissociated into smaller radicals also by electron impact. Moreover, the fluorocarbon radicals CFₓ (x=1-3) recombine with F atoms to form CFₓ₊₁. The equations of F atoms dissociation and recombination are written as

\[
\text{CF}_4 + e \rightarrow \text{CF}_3 + \text{F} + e \quad (1)
\]

\[
\text{CF}_3 + e \rightarrow \text{CF}_2 + \text{F} + e \quad (2)
\]

\[
\text{CF}_x (x=1-3) + F \rightarrow \text{CF}_{x+1} \quad (3)
\]

According to the CF₄ plasma gas-phase reaction process, it can be seen that the CF₄ 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 CF₄ are fluorine atom, fluorocarbon radicals and fluorocarbon ion.

CF₄ plasma generated such as active atoms, ions and free radicals occurred various physical and chemical reactions with the SiO₂ 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 SiO₂ substrates is attributed mainly to reactions through simultaneous exposure of reactive F atoms, the neutral atoms and molecules adsorbed react with the SiO₂ surfaces to form surface reaction layers. The fluorine atoms, fluorocarbon radicals and polymers are bonded to SiO₂ surface sites, gradually forming SiFₓ (x=1-4) and etching of fully fluorinated Si sites SiF₄ and then diffusion away from the surface.

During CF₄ plasma discharge, the F atoms and CFₓ(x=1-3) molecules are generated by high energy ion bombardment, the ionization thresholds of CF is 18eV, while the thresholds of CF₂ is low at 14eV. As the lower efficient collision for excitation, CF₂ is the most abundant molecular radical species present in CFₓ(x=1-3) molecules. The gas-phase CF₂ 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 CF₂ plays a significant role in surface polymerization. For these reasons, it is necessary to investigate the density of F atoms and CF₂ molecules in CF₄ plasma processing with the experimental parameters.

Atomic emission spectroscopy of F and CF₂

The excitation and ionization of CF₄ directly influence the concentration of charged species, which plays a significant role in chemical reaction processing. It is demonstrated that by changing the experimental conditions, e.g. input power, flow rate of CF₄ and gas feed composition, it is possible to change the concentration of F atoms and of CF₂ 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 CF₂ molecules spectra by the key factors of CF₄ plasma including input power, flow rate of CF₄ 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 CF₄ 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.

![Graph showing emission intensity for F and CF₂ species as a function of CF₄ flow rate](image1)

**Figure 1. Emission intensity for F atoms and CF₂ molecules with input power**

According the experimental results, in a CF₄ plasma, relative CF₂ 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 CF₂ molecules.

CF₄ is the provider of F atoms and CF₂ molecules, so the flow rate of CF₄ may affect the plasma spectra greatly. As shown in Fig.2, the emission intensity for F atoms and CF₂ molecules as a function of CF₄. The change trends of F atoms and CF₂ molecules are basically the same, and the spectrum intensity of F atoms is far greater than the intensity of CF₂ molecules.

![Graph showing emission intensity for F and CF₂ species as the flow rate of CF₄](image2)

**Figure 2. Emission intensity for F and CF₂ species as the flow rate of CF₄**

From the spectra curve, it can be seen that the influence on F atoms is more obvious than CF₂ molecules under the condition of constant input power. The emission intensity firstly rises with the increase of CF₄ and then reach a peak value at about 20 ml/min, when the flow of rate of CF₄ exceeds 20 ml/min, both of the emission intensity decrease. However, the emission amplitude of F atoms decreases obviously, and the intensity of CF₂ 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 CF₄ increased, the number of F atoms in the ground state is greater than the number of excited states, which causes the emission intensity decreased.

In the CF₄ plasma processing, O₂ as the auxiliary gas is mixed into CF₄ to increase the intensity of the reactive F atoms and hence speed up the material removal rate. To investigate the effects of O₂ on
the plasma spectra, by changing the ratio of O\textsubscript{2} to CF\textsubscript{4} while keeping other parameters unchanged, the emission intensity for F and CF\textsubscript{2} species as a function of O\textsubscript{2}/CF\textsubscript{4} as Fig. 3.

![Figure 3](image-url)

Figure 3. Emission intensity for F and CF\textsubscript{2} species as a function of O\textsubscript{2}/CF\textsubscript{4}

As can be seen in Fig. 3, the emission intensity of F atoms rises with the O\textsubscript{2} addition, and then reach a peak value at about 20\% of O\textsubscript{2}/CF\textsubscript{4}. It is possible that the intermediate products CF\textsubscript{x}(x=1-3) ionized from CF\textsubscript{4} can easily react with O\textsubscript{2} to produce COF\textsubscript{2}, CO or CO\textsubscript{2}. This process will prevent the active particles in plasma from recombination, and then, more active F atoms are released out. Meanwhile, the CF\textsubscript{2} and O combine prior to desorbing from the surface as CF\textsubscript{2}O, thereby reducing the amount of scattered CF\textsubscript{2}. However, when the O\textsubscript{2} ratio continues increased, the recombination process between O\textsubscript{2} and CF\textsubscript{x} reach adsorption saturation, the excess O\textsubscript{2} will not maintain the activity of F atoms. Thus, the emission intensity of F atoms decreased with high ratio of O\textsubscript{2}/CF\textsubscript{4}. And the emission intensities of F atoms raised and reached the maximum at the O\textsubscript{2}/CF\textsubscript{4} ratio of 20\%.

Conclusions

The chemical reaction involved in the CF\textsubscript{4} plasma was investigated, the two crucial stages of gas-phase reaction in CF\textsubscript{4} plasma and chemical reaction on SiO\textsubscript{2} surface were investigated to reveal the formation mechanism of the surface during APPJ. F atoms and CF\textsubscript{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\textsubscript{2} groups ionized from reaction gas CF\textsubscript{4}. The effects of different atmospheric plasma processing parameters on the ionization of reaction gas CF\textsubscript{4} are studied. The CF\textsubscript{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\textsubscript{2} molecules are basically the same with the increase of CF\textsubscript{4}, and the spectrum intensity of F atoms is far greater than the intensity of CF\textsubscript{2} molecules. Addition O\textsubscript{2} into CF\textsubscript{4} plasma prevented the F atoms from recombination with CF\textsubscript{2} molecules, moreover, the CF\textsubscript{2} molecules reacted with O\textsubscript{2} and produced COF\textsubscript{2}, CO or CO\textsubscript{2}, and reached the maximum at the O\textsubscript{2}/CF\textsubscript{4} ratio of 20\%.

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References


