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Application of Cryoplasma to Ashing Process

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1. Introduction

The demand for increasingly fast computers continues to grow. Up to now, the miniaturization of microprocessors and their key components, transistors, has driven increases in processing speeds. While shrinking dimensions makes transistors faster, it also makes interconnections between transistors work slower. An interconnection can be represented as resistors and capacitors connected in series. Such an interconnection can be characterized by its resistance-capacitance (RC) value. Shrinking the cross-section of a wire increases its resistance and bringing wires closer together increases the capacitance between them. As a result, a signal propagating through the interconnection experiences increased RC delays as the device size decreases. At the same time, the power consumption of the device increases and causes overheating [1].

One innovative approach to solve this problem is to decrease the value of the capacitance, which can be achieved by using low dielectric constant - low-κ - materials [1]. One class of low-κ materials are porous silicon organo silicate glasses (OSG). The lower κ value of porous OSGs when compared to silicon oxide is due to the lower density achieved by a porous structure. For further reducing the κ value, the oxygen atoms in nanoporous OSGs are replaced by F, C, or CH_x, because these groups have less polarity. In typical nanoporous low-κ OSGs, the porosity can reach as much as 90% and the pore sizes typically vary from 2 nm to tens of nanometers.

However, there are difficulties related to the processing of nanoporous OSGs. In oxygen plasma ashing, oxygen radicals originating from the plasma can diffuse through the pores to the inside of the material. The Si-CH_x bonds are then replaced by Si-O, leading to an increase of the κ value [2].

Recently, first attempts have been made to use cryoplasmas for the ashing of low-κ nanoporous OSGs [3]. Cryoplasmas are plasmas whose gas temperature can be controlled below room temperature in a continuous way [4]. Noma *et al.* [5] generated cryoplasmas whose gas temperature could be controlled from 5 to 300 K continuously. Cryoplasmas are expected to be advantageous in various materials processes demanding low temperatures and a high reactivity [4, 5]. In a series of experiments conducted by Iacopi *et al.* [3], the authors used low-κ nanoporous OSG (κ: 2.0, porosity: 40%, pore diameter: around 4 nm) as ashing samples. The gas for generating the plasma and ashing was a mixture of Ar and O_2, the pressure being controlled at 100 Torr [3]. From Scanning Transmission Electron Microscopy-Electron Energy Loss Spectroscopy (STEM/EELS) and X-Ray Reflectivity (XRR) measurements, they found that compared to plasmas generated at room temperature, in plasmas generated at 200 K, the depth that O* radicals could penetrate into the nanopores to attack the surface was decreased by one third [6]. Therefore, cryoplasmas are expected to reduce the oxygen radical damage during the ashing process of low-κ materials.

Iacopi *et al.* [3] mainly focused on the characterization of the low-κ samples after cryoplasma ashing, however, the characteristics of the cryoplasma during ashing has not been investigated yet. In order to further optimize the cryoplasma ashing process, the goal of the present study was to characterize the properties of the cryoplasma by monitoring the plasma species and the *I-V* characteristics of the plasma during ashing. In a second step, the goal was to relate the plasma properties to the characteristics of the low-κ samples

after ashing. In addition to the previously used Ar/O_2 plasmas, we added N_2 to the gas mixture to generate a cryoplasma. According to the research of Kim *et al.* [7], N_2 was found to form a layer that acts as a barrier against the damage from O_2 plasmas during etching.

The goal of this research was to both characterize the ashing cryoplasma and to investigate the ashing performance by adding N_2 to Ar/O_2. In order to prove that cryoplasmas lead to less damage in low-κ materials, in a first time I wanted to show that cryoplasmas can also be applied for the ashing of photoresists. The goal of these experiments was to see whether the cryoplasma could remove the photoresist completely, also at temperatures lower than those used in previous studies. It is expected that the present work will lead to a better understanding of the fundamental properties of cyroplasmas and will help to increase their application in materials processing, especially semiconductor devices fabrication.

2. Experimental Approach

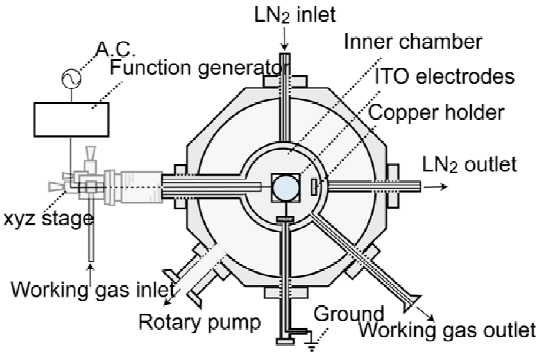

Fig. 1 Schematic of experimental setup Top View of the chamber [5]

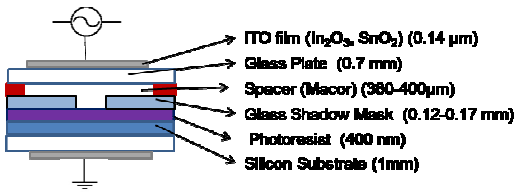

Fig.2 Cross-sectional view of ITO electrodes and photoresist samples

The plasmas were generated in a custom-made chamber (shown in Fig.1), that allowed to control the atmosphere temperature from 78 K to 300 K using liquid nitrogen. I employed dielectric barrier discharge type electrodes, indium-tin-oxide (ITO) deposited on glass substrates being used as electrodes for generating the cryoplasmas [8]. The samples were silicon substrates coated with a 400 nm thick ESCAP (copolymer of poly (t-butyl acrylate) and poly (hy-droxystyrene)) type photoresist [9]. The plasmas were generated at a frequency of 20 kHz and voltages of 0.9-1.8 kV. During the experiments, the gas flow rate was set to 100 sccm Ar and 10 sccm O_2 at a total pressure of 100 Torr [3].When adding N_2 to Ar/O_2, the flow rate was set to 100 sccm Ar, 90 sccm N_2, and 10 sccm O_2 at a total pressure of 100 Torr.

First, I ashed the photoresist samples at room temperature for 5, 10, and 20 min, at 240 K for 5, 10, 20, and 40 min, at 170 K for 5, 10, 20, 40 and 70 min. In addition to these experiments, I also conducted *I-V* measurements during each ashing experiment. Additionally, optical emission spectra were acquired for identifying the species in the plasma. For the characterization of the samples after ashing, the surfaces of the ashed samples and a non-ashed sample were investigated by X-ray photoelectron spectroscopy (XPS). From the data of XPS, we can see the change of element composition on the surface of the samples depending on different ashing temperature and ashing time, in order to optimize the ashing time and temperature necessary to completely ash the photoresist. Second, I ashed the photoresist samples adding N_2 to the Ar/O_2 gas mixture. The ashing experiments were conducted for a duration of 20 min at room temperature, 40 min at 240 K and 170 K, 80 min at 170 K. Both *I-V* and XPS measurements were conducted for each sample, and OES measurement of 170 K/70 min ashing. Finally, these data could help us to optimize the ashing process of the photoresist by adjusting the temperature of the plasma gas, the ashing time and the plasma conditions (i.e. voltage and frequency).

3. Experimental Results

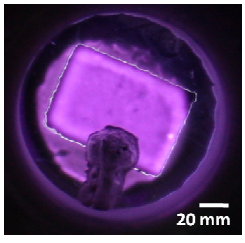

Fig.3 Photograph of Ar/O_2 plasma during generation at 170 K

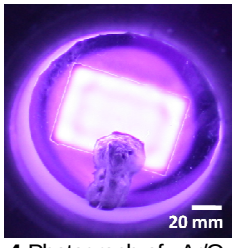

Fig.4 Photograph of Ar/O_2+N_2 plasma during generation at 170 K

From the I-V curve shown in Fig. 5, we could confirm the generation of the plasma, the discharge was filament mode. The power consumption of the Ar/O_2 ashing plasma as estimated from the *I-V* curves was about 0.32 W to 0.40 W. The optical emission spectra presented in Fig. 6 show lines that originate mainly from Ar. When adding N_2 to the Ar/O_2 plasma, the peaks are mainly due to N_2.

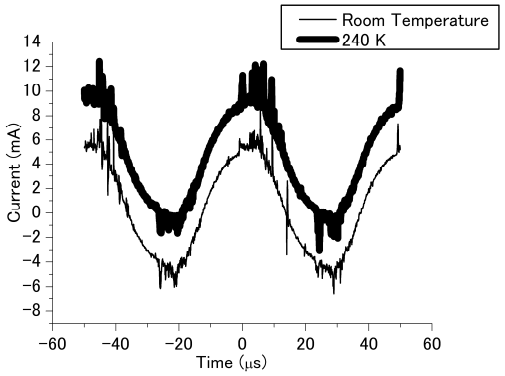

Fig.5 Current curve of the Ar/O_2 ashing plasma

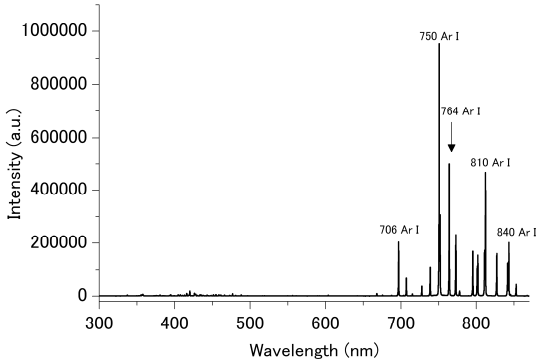

Fig.6 OES result of Ar/O_2 ashing plasma

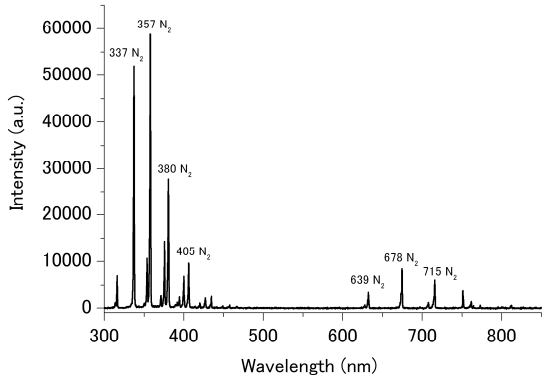

Fig.7 OES result of $Ar/O_2 + N_2$ ashing plasma at 170 K

Table.1 Variation of atomic concentrations of C and Si at the surface of the ashed samples estimated by XPS.

	C (1s) %	Si (2p) %	Ashing Rate
No ashed	81.65	1.36	
240 K & 20 min	33.39	20.7	3.33
240 K & 40 min	10.88	37.79	2.23
170 K & 20 min	78.53	1.66	1.07
170 K & 70 min	20.39	33.5	1.13

From the values listed inTable.1, it can be seen that both at 240 K and 170 K, the atomic concentration of Si from the sample substrate increased as the ashing time increased. On the other hand, the concentration of C from the photoresist on the surface of samples decreased. The ashing rates are expressed in at % C per minute. It can be seen that at 240 K ashing is more efficient than at 170 K.

4. Conclusions

Photoresist-coated Si substrates were ashed by cryoplasmas generated at temperatures ranging from RT to 170 K. From XPS measurements of the samples it was found that for lower cryogenic temperatures, longer ashing times are necessary to remove the photoresist completely. However for gaining a deeper understanding of the mechanisms resulting in the removal of the photoresist and to optimize the cryoplasma ashing process, more detailed investigations are necessary. The goal is to relate the plasma properties (plasma chemical composition, plasma generation parameters, active species in the plasma) to the ashing mechanisms. Finally, it is expected that these data will serve as a reference to the application of cryoplasmas for the ashing of low-κ and other materials used in semiconductor devices.

5. Reference

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