# Characteristics of the Oxygen Plasma and Its Application to Photoresist Stripping

## (산소 플라즈마의 특성과 포토레지스트 제거에의 응용)

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### 要 約

에칭공정과 포토레지스트 제거에 이용되는 RF방전의 물리적 현상과 원리는 잘 이해되고 있지않고 있으며 플라즈마 반응기구의 설계와 플라즈마 기계의 최적 운용조건의 결정은 대체적으로 실험적인 경험에 기반을 두고 있다. 본 논문에서는 방전현상을 플라즈마 특성의 측정을 통해서 분석했으며 그 분석의 결과를 포토레지스트 제거현상에 적용시켰다. 또 플라즈마 전자의 밀도, 중성산소 기체압력과 전극온도가 포토레지스트 제거율에 미치는 영향을 살펴보고 플라즈마의 특성으로부터 그 현상들을 이해했다. 이 연구는 건식에칭에 관련된 공정에도 적용될 수 있다.

### Abstract

The physical mechanism of a RF discharge used in photoresist stripping and etching process are not well understood and, the plasma reactor design and the determination of optimum operating coditions are done largely on empirical basis. We analyzed the discharge process through the measurement of plasma characteristics and applied our results tothe analysis of the photoresist stripping. We investigated the effects of plasma electron density, neutral oxygen gas pressure and electrode temperature on the stripping rates and related their effects with the characteristics of plasma.

## I. Introduction

The plasma technology seems to have first been applied to the integrated circuit processes during the 1960' as plasma stripping, also known as the plasma ashing.[1] This is a technique for the removal of the photoresist materials which, being organic, consist essentially of carbon and hydrogen. Solid carbon is converted to gaseous carbon monoxide and dioxide by oxidation in an oxygen gas discharge. Gas discharge processes in environmental legislation, employee-safety regulations and, IC packing densities have all favored dry process technology.

But up to now, the characteristics of the plasma has not been discussed throughly in its application. In this paper we discuss the discharge process and the characteristics of oxygen plasma. First we analyze the breakdown phenomena of oxygen gas and introduce the electrical circuit model of the plasma. And we also introduce the diagnostic technique with the results of measurement. After the analysis of the plasma characteristics we investigated the effects of the plasma electron density,

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oxygen gas pressure and electrode temperature, on which the wafers are loaded, on the stripping rate. The experimental data are consistent with our anticipation based on the analysis of plasma characteristics. The work described in this paper was undertaken in order to get a better understanding of discharge and stripping process, although the considerations are applicable to the etching process as well.

Our planar discharge system is shown in Fig. 1. The upper electrode is the powered electrode, while the wafers are loaded on the grounded electrode. The plasma is largely confined to the region between the electrodes and the gas is introduced into the reactor through the powered electrode. The RF power of 13.56 MHz is applied to the plasma through the L-Matching network.[2] We used a Langmuir probe[7] to measure the plasma parameters. The temperature of the wafers influences the photoresist stripping rate through the effect on the rates of chemical reaction. Heating by the plasma is a major source of temperature rise. Thus some means of substrate temperature control is necessary to obtain uniform and reproducible stripping rate, and we adopted water cooling system.

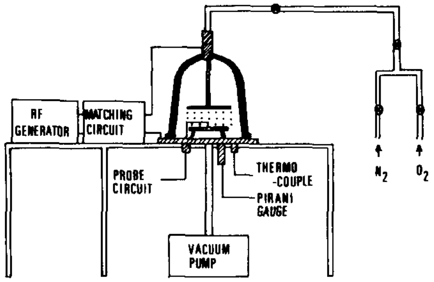

Fig. 1. Discharge system;glass chamber, stainless electrode of 4cm radius, electrode distance 4cm, 100W RF generator of 13.56MHz, Tungsten wire probe of 0.15mm insulated by glass.

We use 13.56 MHz RF field to produce the plasma. The advantages of RF discharge are such that it can be sustained independent of the yield of secondary electrons from the walls and electodes, the possibility of ionizing collisions is enhanced by electron collisions allowing operation at low pressures and electrodes within the discharge can be covered with insulating materials.

## II. Discharge Process and Its Properties

Plasma-assisted semiconductor techniques rely on partially ionized gases consisting of ions, electrons, and neutrals produced by low pressure electric discharge. When an electric field of sufficient magnitude is applied to a gas, the gas breaks down and the discharge reaches a self-sustained steady state when electron generation and loss processes balance each other.

In our system the main loss mechanism is the diffusion process and the breakdown voltage can be calculated from the condition of balance between diffusion and ionization. The computed data[3] are compared to the experimental data and our prediction is roughly consistent with the experiment as shown in Fig. 2.

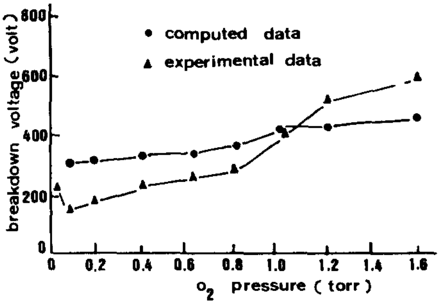

Fig. 2. Breakdown voltoge.

When the neutral gas pressure is lower than 0.1 Torr, the breakdown voltage increases as the neutral gas pressure decreases. This can be understood by the fact that, at low pressure, the collisions between electrons and oxygen atoms or molecules are not sufficient for the breakdown because of low density of neutral particles. Thus, as the gas pressure decreases, the breakdown voltage increases. On the other hand, when neutral gas pressure is greater than 0.1 Torr, the breakdown voltage increases as the neutral gas pressure increases. As the neutral gas pressure increases, the mean free path of electron becomes shorter and thus the kinetic energy absorbed by the electron from the oscillating field becomes small and so does the ionization rate.

In the Langevin model[4], it is assumed that the electrons are free to move in a stationary uniform background of ions and neutrals which provide the collisional damping force. Langevin equation for the electron motion is as follows,

$$d/dt\,(M\vec{u}) = -e\vec{E} - M\vec{u}\upsilon_m \tag{1}$$

where M, $\vec{u}$, e are the mass, velocity and charge of electron, $\vec{E}$ is the electric field, where, $\upsilon_m$ is defined as collision frequency for the momentum transfer.[4]

This model gives the conductivity and dielectric constant of palsma as,

$$\sigma = \frac{ne^2\,\upsilon_m}{M(\upsilon_m^2 + \omega^2)} - j\,\frac{ne^2}{M(\upsilon_m^2 + \omega^2)} \tag{2}$$

$$\epsilon = \epsilon_0\left(1 - \frac{\omega_p^2 \,/\, \omega^2}{1 - j\upsilon_m/\omega}\right), \quad \omega_p = \frac{ne^2}{M\,\epsilon_0} \tag{3}$$

where $\omega_p$ is the plasma frequency.

Generally speaking, a complex dielectric constant simply implies a lossy dielectric, i.e. in which an electromagnetic wave is attenuated as it propagates. The degree of attenuation, however, depends upon the frequency of the wave, or more accurately, the ratio, $\upsilon_m/\omega$. The equations obtained for the conductivity and dielectric constant, even though very simple, are very useful. We used the above quantities to find out the equivalent circuit model of plasma system and utilized this model to design the matching circuit.[5,6]

## III. Measurement of Plasma Conditions

We used Langmuir probe technique to measure the plasma conditions which is one of the fundamental technique for the determination of plasma properties.[7] It consists of a tungsten wire of radius 0.15mm, insulated by glass.

Fig. 3 shows the dependence of the electron density of plasma on the applied RF power. Since.

$$P_{diss} = \sigma_{real}\, E^2 \tag{4}$$

$$\sigma_{real} = P_{diss} \,/\, E^2 \tag{5}$$

where E is electric field strength, and conductivity of plasma is linearly dependent upon the plasma electron density as shown in Eq.(12), it is reasonable for the electron density to increase with RF power.

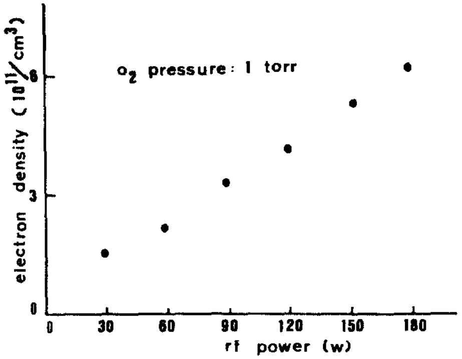

Fig. 3. Electron density as a function of RF power.

Fig. 4 shows the relation between electron density and neutral gas pressure. The mean free path of the electron decreases as the neutral gas pressure increases. But the decrease of the mean free path in the gas pressure 0.5-2 Torr, is not sufficient enough to influence the ionization rate. The decrease of the mean free path of the electron, so the decrease of electron energy received from the applied RF field between collisions is compensated by the increase of ionizable neutral particle density. Thus the electron density varies negligibly as the neutral gas pressure changes in the neutral gas pressure 0.5-2 Torr.

We have measured the electron density and temperature based on the assumption of electron's Maxwellian velocity distribution. In many plasma analysis, the electron density of plasma is assumed to be equal to the ion density. But temperature of the electron is

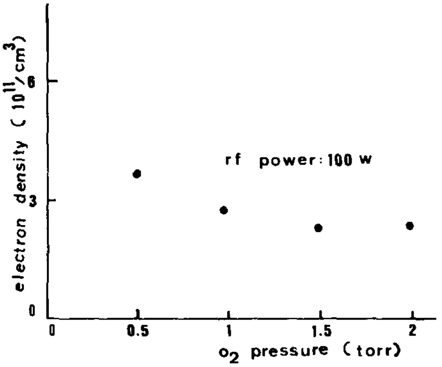

Fig. 4. Electron density as a function of gas pressure.

thought to be higher than that of ion, because of their mass difference. Fig. 5 shows the relation between electron temperature and the applied RF power. If the RF power increases the oscillating electric field strength increases and so does the energy absorbed by the electron from the field. But the density of electron, thus the ionizing nonelastic collision rate, and photon energy emitting from the plasma become larger. Thus the net effect of the applied RF power increase does not influence the electron energy significantly.

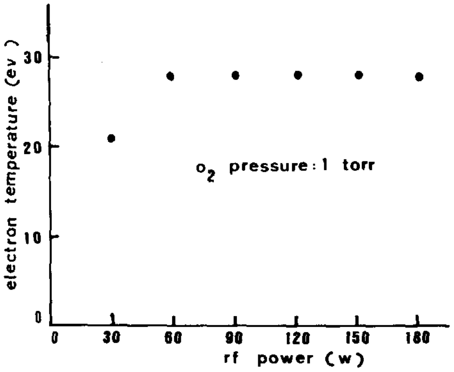

Fig. 5. Electron temperature as a function of applied RF power.

Fig. 6 shows the relation between the electron temperature and neutral oxygen gas pressure. At lower pressures, the electrons under go fewer collisions with neutral particlies, which are oxygen molecules and atoms in oxygen plasma as reported,[8,9] thus accumulating larger kinetic energy from the field. Hence as the gas pressure increases, the electron energy decreases.

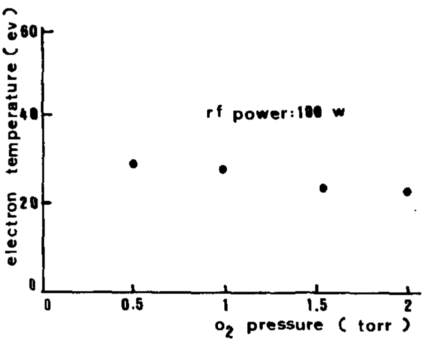

Fig. 6. Electron temperature as a function of oxygen gas pressure.

## IV. Stripping Experiment and Its Results

Photoresist removal occurs through an oxidation reaction where in the photoresist ($C_xH_y$) *combines with active oxygen* as follows.

$$C_xH_y + O_2 \rightarrow CO\uparrow + CO_2\uparrow + H_2O\uparrow$$

The products produced by this reaction are removed from the plasma chamber by a vacuum pump. In this work, wafers are loaded on the grounded electrode and the vacuum chamber begins to be pumped down: The oxygen is then bled into the chamber and RF field is turned on at the same time, which is capacitively coupled to the gas at a fixed frequency of 13.56MHz. The RF power exciter the oxygen, creating the active species, as mostly atomic oxygen, which reduce the resist's polymeric chains to simpler and lower-molecular-weight groups. These then volatilize and leave the system.

First, we carried out an experiment to find out the relation between the applied RF power and the photoresist stripping rate using A2-1350J positive phot-resist which was hard back we measured photoresist thickness by Nanospec and results are shown in Fig. 7 and Fig. 8. The stripping rate increases as RF power, as we can expect, for both positive and negative photoresist material. Since the density of the electron in plasma increases with RF power, the number of oxygen atom also increases by the collisions between the electrons and oxygen molecules. At oxygen gas pressure 1.0 Torr, RF power 80W, and electrode temperature 70°C the stripping rate is about 1000 Å/min.

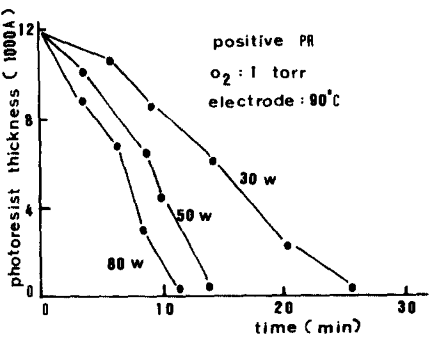

Fig. 7. Stripping rates of positive PR on RF power variation.

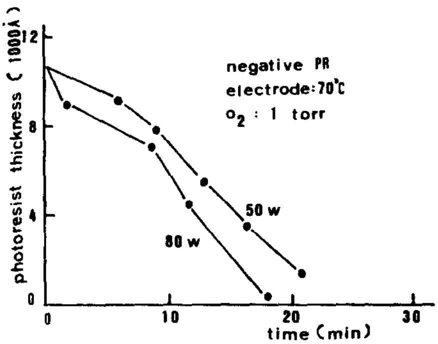

Fig. 8. Stripping rates of negative PR on RF power variation.

Secondly, we examined the effect of electrode temperature variation on the stripping rate. The grounded electrode where the wafers rest on is water-cooled and the temperature of the electrode is controlled by adjusting the flow rate of water. Fig. 9 and Fig. 10 show that the stripping rate increases with the increases of wafer temperature.

We also examined the effect of the neutral gas pressure variation (0.5 ~ 2 Torr) on the photoresist stripping rate, but no dependence was found.

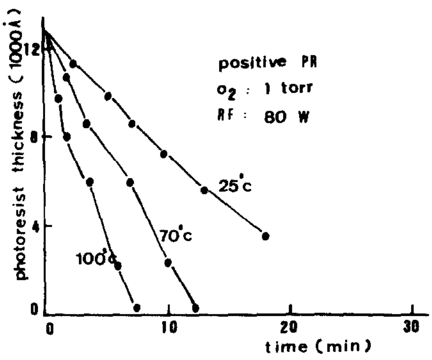

Fig. 9. Stripping rates of positive PR on electrode temperature variation.

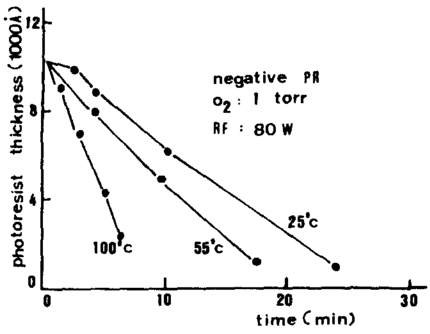

Fig. 10. Stripping rates of negative PR on electrode temperature variation.

## V. Conclusion

We measured the properties of the oxygen plasma and analyzed the data. The breakdown phenomena follows the Paschen law[10] and minimum breakdown voltage exist around the oxygen gas pressure of 0.1 Torr. The density of plasma electron is linearly dependent upon the applied RF power, but is not closely related to the neutral gas pressure. But electron temperature decreases as the neutral gas pressure increases. Such a phenomena can be understood from the fact that the mean free path of the electron becomes shorter since the number of neutral particles increases in the neutral gas pressure

0.5-2 Torr.

The stripping rate was found to be about 1000 Å/min with RF power of 80W, electrode temperature of 70°C and the oxygen gas pressure of 0.1 Torr. Increase of the RF power and electrode temperature both resulted in the increase of the stripping rate.

## References

[1] S.M. Irving, "A dry photoresist removal method," *in Proceedings of Kodak Photoresist Seminar,* vol. 2, pp. 26-29, 1968.

[2] B. Chapman, *Glow Discharge Process,* John Wiley & Sons, Inc., 1980.

[3] K.W. Whang, J.H. Kim, Y.S. Noh, and W.K. Kim, *Breakdown Phenomena of Oxygen Plasma.* in the Conference of Korean Institute of Electrical Engineering, June, 1985.

[4] B.E. Cherrington, *Gaseous Electronics and Gas Lasers,* Pergamon Press, 1979.

[5] K.W. Whang, J.H. Kim, Y.S. Noh, and W.K. Kim, *Impedence Characteristics of $N_2$ Plasma and Matching Circuit Design.* in the Conference of Korean Institute of Electrical Engineering, June, 1985.

[6] J.S. Logan, N.M. Mazza, and P.D. Davidse, "Electrical Characterization of Radio Frequency Sputtering Gas Discharge," *J. Vacuum Science Technology,* vol. 6, no. 1.

[7] R.H. Huddleston, *Plasma Diagnostic Techniques,* Academic Press Inc., 1965.

[8] J.F. Battey, "Design Criteria for Uniform Reaction Rates in an Oxygen Plasma," *IEEE Trans. Electron Devices,* ed-24, pp.140, 1977.

[9] J.F. Battery, "The reduction of photoresist stripping rates in an oxygen plasma by byproduct inhibitation and thermal mass," *J. Electrochem. Soc.,* vol. 124, pp.147, 1977.

[10] Essam Nasser, *Fundamentals of Gaseous Ionization and Plasma Electronics,* John Wiley & Sons, Inc., 1971.