Extended Abstracts of the 16th (1984 International) Conference on Solid State Devices and Materials, Kobe, 1984, pp. 459-462

Invited

ECR Plasma CVD Process

Seitaro Matsuo

Atsugi Electrical Communication Laboratory, NTT

Atsugi-shi, Kanagawa 243-01, Japan

A low temperature chemical vapor deposition (CVD) process utilizing an electron cyclotron resonance (ECR) plasma has been developed. The ECR plasma CVD process can deposit dense and high quality thin films, such as Si_3N_4 and SiO_2, without substrate heating. The deposition reaction is enhanced by using a microwave ECR plasma excitation at low gas pressures of 10^{-4} Torr, and an ion extraction in the form of plasma stream by a divergent magnetic field, which bring about highly activated plasma and ion bombardment with moderate energy of about 20 eV, respectively. The Si_3N_4 and SiO_2 films deposited are comparable to those prepared respectively by high temperature CVD and thermal oxidation, in evaluations such as by buffered HF solution etch rate measurement.

1. Introduction

Plasma CVD (chemical vapor deposition) technique, which employs plasma reactions by RF (radio frequency) discharge, has become an important research subject as a low temperature process in recent years.[1-3] A deposition technique using a microwave discharge and a plasma transport at a low gas pressure with a parallel magnetic field has also been reported.[4] In both these techniques, the substrate must still be heated to a temperature of from 250 to 350 °C. Furthermore, the quality of the deposited film is inadequate, possibly because raw material gases, such as SiH_4, do not sufficiently decompose, and the reaction during deposition is not complete. These might allow hydrogen and poor molecular bonds to remain in the film.

The ECR plasma CVD process developed in this study allows deposition of dense and high quality thin films without substrate heating. These characteristics are brought about by enhancing the plasma excitation efficiency and by the acceleration effect of ions, using the ECR plasma,[5-7] and a plasma extraction by a divergent magnetic field.

2. ECR Plasma Deposition Apparatus

Figure 1 illustrates the ECR plasma deposition apparatus.[8] Microwave power is introduced into the plasma chamber through a rectangular waveguide and a window made of a fused quartz plate. Microwave frequency is 2.45 GHz, and output power is delivered at 50 Hz duty cycle, at the convenience of a power supply. The plasma chamber is 20 cm in diameter and 20 cm in height in inside dimensions and operates as a microwave cavity resonator (TE_{113}). Magnet coils are arranged around the periphery of the chamber for ECR plasma excitation. The circular motion frequency, electron cyclotron frequency, is controlled by the magnet coils so as to coincide with the microwave frequency (magnetic flux density, 875 GHz) in a proper region inside of the chamber. These designs are similar to those of the broad-beam ECR

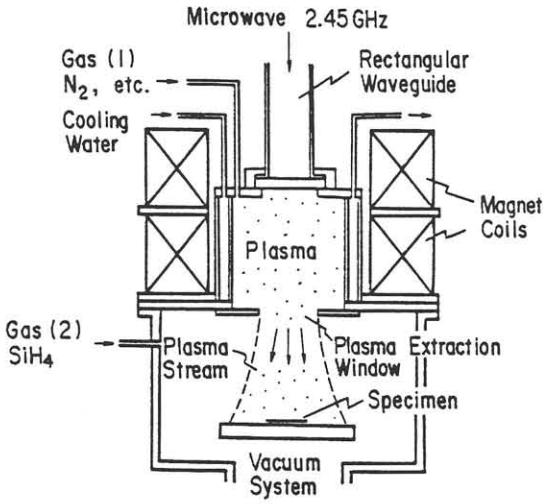

Fig. 1. ECR plasma deposition apparatus. Substrate, without heating. Gas pressure, about 10^{-4} Torr.

ion source previously reported.[8] The ECR condition enables the plasma to effectively absorb the microwave energy. Thus, highly activated plasma is easily obtained at low gas pressures of 10^{-5} to 10^{-3} Torr.

In this apparatus, ions are extracted in the form of plasma stream from the plasma chamber to the specimen chamber, along a divergent magnetic field, to deposit a film on the specimen substrate. Reactive deposition gases are introduced through two inlet systems, one into the plasma chamber and the other into the specimen chamber. The plasma chamber and the magnet coils are water-cooled. The vacuum system consists of an oil diffusion pump (2400 l/sec) and a mechanical rotary pump (500 l/min).

3. Divergent Magnetic Field Ion Extraction

A divergent magnetic field method has been developed for ion extraction in the form of plasma stream from the plasma chamber to the specimen chamber. The intensity of the magnetic field in the specimen chamber is gradually weakened from the plasma chamber to the specimen table, as shown in Fig. 2. High energy electrons in circular motion peculiar to ECR plasma are accelerated by the interaction between their magnetic moments and the magnetic field gradient. The accelerated electrons bring about a negative potential toward the specimen table which is electrically isolated from the plasma chamber. Therefore, a static electric field, which accelerates ions and decelerates electrons, is generated along the plasma stream so as to satisfy the neutralization condition. The effective ion extraction and transport to the specimen surface with a moderate energy are thus enhanced during deposition.

The potential ϕ in the plasma stream is given, under these conditions, by

$$\phi = -(W_0/e)(1 - B/B_0),$$

where B is the magnetic flux density, e is the charge, and W_0 and B_0 are the electron energy and the magnetic flux density in the plasma chamber. This equation states that the ion energy is approximately given by the product of the electron energy in the plasma chamber and the ratio of the decreased magnetic field intensity to the initial. Ions are thus accelerated and transported toward the specimen table, and electrons lose the energy of circular motion by the same amount. As a result, deposition reactions induced by ions are enhanced, and heating effects caused by electrons are reduced.

The negative potential generated by the divergent magnetic field was measured using a plane probe from its floating potential. The obtained result is shown in Fig. 3 as a function of the distance from the plasma extraction window. The negative potential increases, corresponding to the decrease in the magnetic field intensity.

The plasma potential along the plasma stream was measured directly using an emissive probe

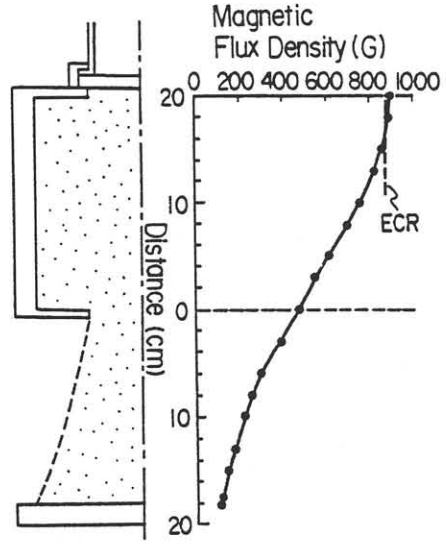

Fig. 2. Distribution of magnetic field intensity from top of plasma chamber to specimen table.

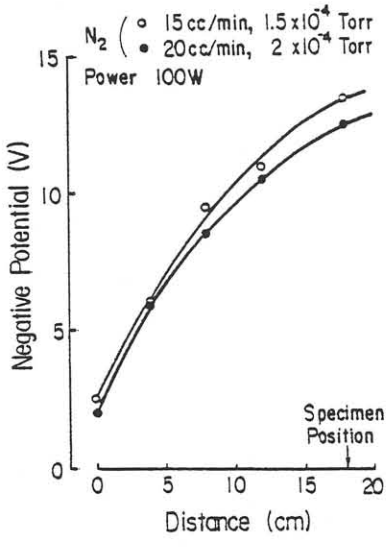

Fig. 3. Negative potential generation by divergent magnetic field method.

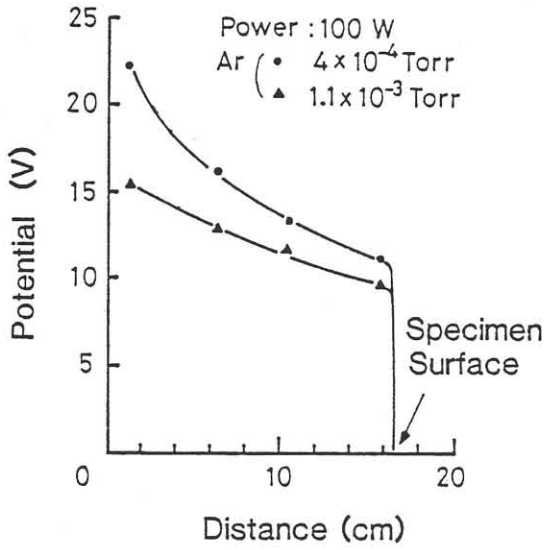

Fig. 4. Plasma potential along plasma stream.

method,[10] in order to distinguish from each other the respective effects of the electric field in the plasma stream, and the electric field due to the ion sheath on the specimen surface generated by the thermal motion of electrons parallel to the magnetic field. The results are shown in Fig. 4, where the substrate potential is chosen as zero. The voltage due to the ion sheath (about 0.3 mm in thickness) is about 10 V. The ion energy incident to the specimen surface is given by the sum of the energy gained in the divergent magnetic field and that due to the ion sheath voltage, and is about 20 to 30 eV. The ions in such an energy range are expected to enhance deposition reactions and to improve the film quality, but not to cause surface damages. High ion current density of 3 to 5 mA/cm^2 is obtained at the specimen table.

4. Deposition Characteristics

All the experiments on film deposition were carried out without substrate heating. The specimen temperature was in the range from 50 to 150 ^{o}C, due to some heating effect by the plasma. Deposition area is 20 cm in diameter, and the uniformity is within ± 5 % in the 10 cm diameter middle area.

For silicon nitride (Si_3N_4) film deposition, nitrogen (N_2) and silane (SiH_4) gases are introduced into the plasma chamber and the specimen chamber, respectively. Figure 5 shows the Si_3N_4 deposition characteristics as a function of microwave power, when the introduced gas flow rates are N_2, 30 cc/min and SiH_4, 20 cc/min. The deposition rate increases upto about 700 Å/min, and the refractive index markedly decreases with microwave power to 150 W, and then becomes almost constant. This means that the microwave power larger than 150 W is required for sufficiently complete reactions to deposit Si_3N_4 film in this condition. Figure 6 shows the internal stress of the films, also as a function of microwave power. The stress is compressive for the main, but becomes tensile to some extent at the power of about 150 W. This tendency seems to be related to the variation of refractive index in Fig. 5. The internal stress of the Si_3N_4 film can be thus controlled to about zero. The film stress

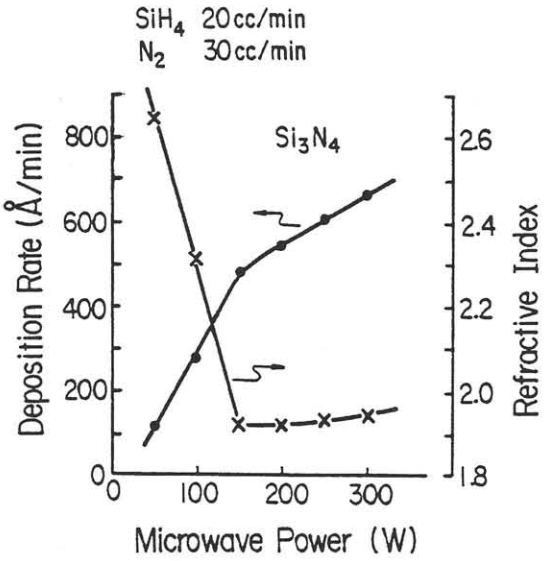

Fig. 5. Si_3N_4 deposition characteristics.

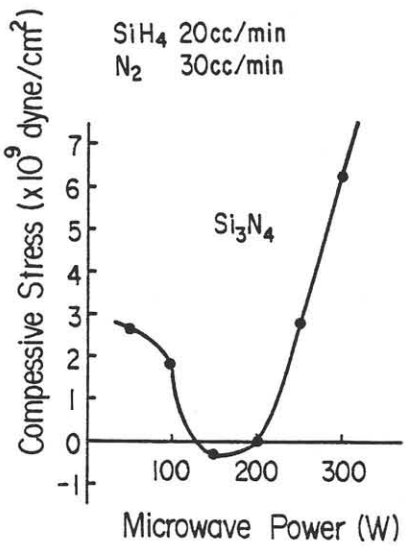

Fig. 6. Internal stress of deposited Si_3N_4 films.

controllability is very advantageous for various applications.

The infrared absorption spectra for the Si_3N_4 films were examined. Consequently, the Si-N bond peak is clearly observed at the wave number of 845 cm^{-1}, while the Si-H bond peak at about 2100 cm^{-1} is hardly observed. The amount of hydrogen in the films seems very small.

The etch rates of the Si_3N_4 films with a buffered HF solution (BHF, 50% HF : 40% NH_4F = 15 : 85, 20 °C) were further examined for film quality evaluation. These rates are shown in Fig. 7 as a function of the film refractive index, which was changed by controlling the ratio of the introduced gas flow rates of N_2 and SiH_4. The etch rate reaches the minimum value at the refractive index of about 2.0. The value there is lower than 10 Å/min, which is comparable to those of the high temperature (800 °C) CVD films, in spite of the deposition at a low temperature without substrate heating.

Silicon dioxide (SiO_2) can also be deposited by introducing oxygen (O_2) and silane (SiH_4) gases into the plasma and specimen chamber, respectively. Figure 8 shows the SiO_2 deposition characteristics as a function of microwave power, when the introduced gas flow rates are O_2, 30 cc/min and SiH_4, 30 cc/min. High deposition rate over 1000 Å/min is obtained, and the refractive index is almost constant in a wide range of power.

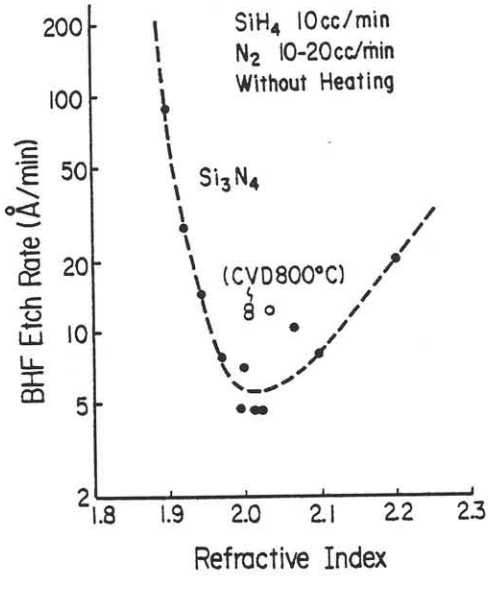

Fig. 7. Si_3N_4 film etch rates with BHF solution. BHF, 50%HF:40%NH_4F = 15:85, 20°C.

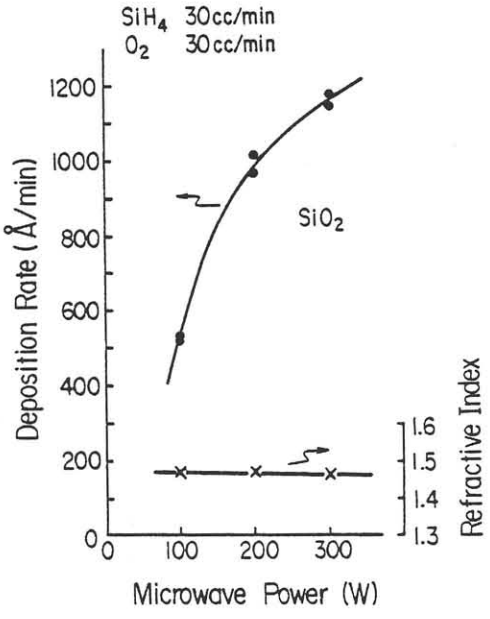

Fig. 8. SiO_2 deposition characteristics.

The etch rates of the SiO_2 films with the buffered HF solution were examined and compared with the SiO_2 film prepared by a thermal oxidation method (wet, 1000 °C). Consequently, the etch rates of the films almost coincide with each other at various solution temperatures.

In conclusion, the ECR plasma CVD process can deposit dense and high quality films, such as silicon nitride and silicon dioxide, without substrate heating. The technique can be applied not only to silicon LSI, but also to compound semiconductor and other heat-sensitive material device fabrication processes, utilizing the advantage of the low temperature process.

References

1) A. K. Sinha, H. J. Levinstein, T. E. Smith, G. Quintana, and S. E. Haszko: J. Electrochem. Soc., 125 (1978) 601.
2) W. A. Lanford and M. J. Rand: J. Appl. Phys., 49 (1978) 2473.
3) A. C. Adams, F. B. Alexander, C. D. Capio, and R. E. Smith: J. Electrochem. Soc., 128 (1981) 1545.
4) T. Tsuchimoto: J. Vac. Sci. Technol., 15 (1978) 70.
5) R. Bardet, T. Consoli, and R. Geller: Fusion Nucleaire, 5 (1965) 7.
6) Y. Sakamoto: Jpn. J. Appl. Phys., 16 (1977) 1993.
7) R. Geller, N. Hopfgarten, B. Jacquot, and C. Jacquot: J. Plasma Phys., 12 (1974) 467.
8) S. Matsuo and M. Kiuchi: Jpn. J. Appl. Phys., 22 (1983) L 210.
9) S. Matsuo and Y. Adachi: Jpn. J. Appl. Phys., 21 (1982) L 4.
10) R. F. Kemp and J. M. Sellen,Jr: Rev. Sci. Instrum., 37 (1966) 455.