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Growth and Properties of Dielectric Thin Films by Microwave-Excited Plasma

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Dielectric thin films such as a silicon nitride and a silicon dioxide have been grown using microwave-excited plasma. Silicon nitride films deposited from microwave-excited N_2 and unexcited SiH_4 have a composition nearly the stoichiometric value in the wide range of experimental conditions, and have a good electrical properties. Moreover, oxidation of silicon surfaces at 600 °C have been performed using microwave-excited O_2-N_2. It is found that the interface property of Si-SiO_2 is as good as that for thermal oxides.

1. Introduction

Development of low temperature growth techniques of dielectric thin films is one of the most important subjects in VLSI fabrication technology. Plasma-enhanced chemical vapor deposition (PECVD) is one of the low temperature techniques and has been extensively studied. In the conventional PECVD, which employs plasma reactions by radio-frequency (RF) discharge, substrates are usually introduced into the discharge region, and hence exposed to the plasma containing high-energetic particles such as electrons, ions and photons. In addition, it is difficult to avoid the incorporation of impurities sputtered from electrodes into the films. Recently, several attempts to reduce the radiation damage have been reported.[1),2)] On the other hand, the thin film growth methods using microwave-excited plasma have been also reported.[3)-6)] One of the advantages of using microwave-excited plasma is that the discharge region can be separated from the reaction region, which results in being free from radiation damage.

In this paper, we report on low temperature growth of silicon nitride (SiN_x) films and low temperature oxidation of Si by a method using microwave-excited plasma and on properties of the films. In this method, substrates are separated from the discharge region and reactant gases such as N_2 and O_2 are excied in a plasma chamber.

2. Experimental

Figure 1 shows a schematic diagram of the experimental apparatus with a microwave-exciting plasma chamber and a reaction chamber. A 2.45 GHz microwave, generated by a magnetron, is guided through a rectangular waveguide to the plasma-exciting chamber made of a quartz tube. The diameter of the quartz tube is 32 mm. The distance between the center of discharge region and the substrates is about 300 mm. The reaction and plasma chambers can be evacuated to 1×10^{-7} Torr using a tarbo-molecular pump.

N_2 and O_2 gases are excited in the plasma chamber and diffused toward the reaction chamber. SiN_x films were deposited on Si wafers by the reaction between unexcited SiH_4 (20 % diluted in N_2) and microwave-excited N_2 (or N_2-Ar mixture)

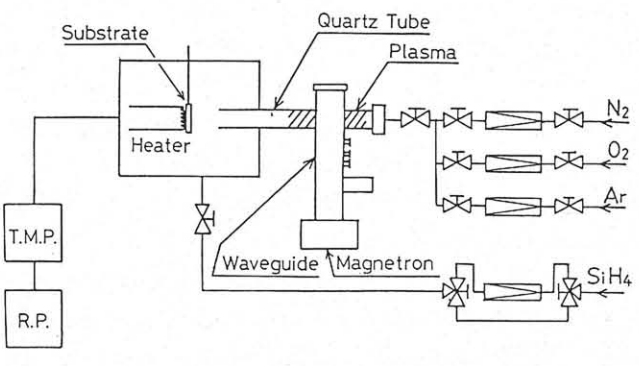

Fig.1 Schematic diagram of experimental apparatus.

gases. SiO_2 films were grown by oxidation of Si surfaces using microwave-excited O_2-N_2 mixture.

3. Results and discussions

Figure 2 shows deposition rates and composition ratios of N/Si obtained by Auger analysis versus gas flow ratio of SiH_4/N_2 under the condition of constant total pressure. In this experimental condition the deposition rate increases with increasing the gas flow rate of SiH_4. On the other hand, it is found that the SiN_x films deposited have nearly the stoichiometric composition (x=1.33) over the wide range of the gas flow ratio. The similar result has been also reported by Shibagaki et al..[3] Figure 3 shows deposition rates and composition ratios versus substrate temperature. It can be seen that the film composition is not affected by the substrate temperature, except for the film deposited at room temperature. In general, the composition of films deposited by the conventional RF-excited PECVD strongly depends on the deposition conditions such as substrate temperature, gas flow ratio and RF power. As seen in Figs. 2 and 3, the composition of the SiN_x films deposited by this method depends less on those deposition conditions. These results show the distinctive feature of this method.

Etching rates in buffered HF solution at 17.5°C for the films deposited at 20-600°C are shown in Fig. 4. The etching rate decreases with increasing the substrate temperature and is of ~4A/min at a substrate temperature of 600°C, the value of which is as small as that of thermal CVD Si_3N_4 films deposited at ~900°C. The values of etching rate for the films are smaller than those for the films deposited by the RF-excited PECVD from SiH_4-NH_3[7] and are comparable to those from SiH_4-N_2.[8] The decrease in etching rate could be attributed to decreasing hydrogen concentration and/or to increaseing density. This result would be attributed to lower hydrogen concentration.

A typical I-V characteristic of the SiN_x films is shown in Fig. 5. The linear relationship between the current density and the square root of electric field at electric fields higher than 4×10^6 V/cm suggests that the Poole-Frenkel's conduction is dominant. The dynamic dielectric constants obtained from I-V characteristics are 3-

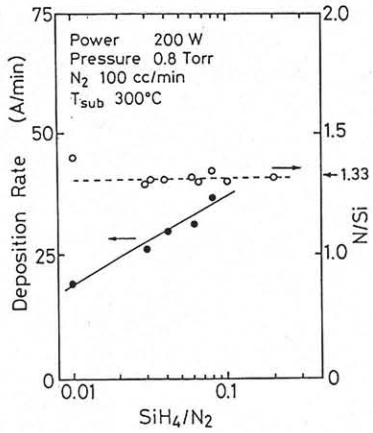

Fig.2 Deposition rates and composition ratios of N/Si for SiN_x films as a function of gas flow ratio of SiH_4/N_2.

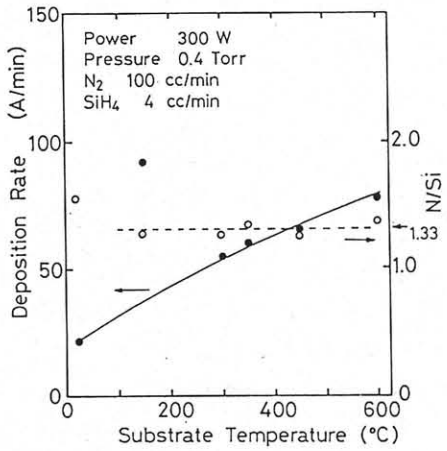

Fig.3 Deposition rates and composition ratios of N/Si for SiN_x films as a function of substrate temperature.

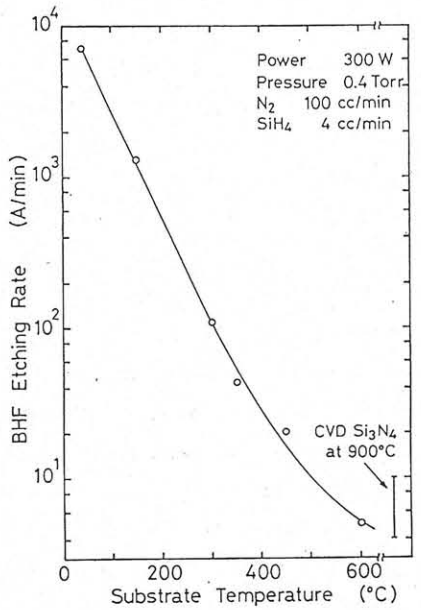

Fig.4 Etching rates in buffered HF solution at 17.5°C for SiN_x films as a function of substrate temperature.

4, which are higher than those of the films deposited by the RF-excited PECVD.[9] Resistivity of the films deposited at 20-600°C is shown in Fig. 6. The substrate temperature has significant influence on the film resistivity, which is similar to the results of etching rate in Fig. 4. The SiN_x films deposited by this method have the resistivity ranging from 10^{15} to 10^{18} Ω-cm at substrate temperatures above 150°C. For the breakdown strength of these films, which is defined a electric field where the current density exceeds 1.7×10^{-3} A/cm^2, the values higher than 6×10^6 V/cm were obtained. On the other hand, the resistivity of the film deposited at 20°C is extremely small. This can be improved by the addition of Ar gases. The value of the film deposited using N_2-Ar mixture excited by microwave power is also plotted in Fig. 6. This result suggests that metastable Ar atoms (and Ar ions) cause to increase the number of radicals and ions in reactant species via inelastic collisions.

It can be expected that ions with appropriate energy enhance the deposition reactions and improve the film quarity. In this method we can control the energy of ion species independent of the discharge condition. Figure 7 shows the deposition rates, the etching rates and the substrate current densities versus bias voltage applied to the substrate. The results in Fig. 7 indicate for the films deposited using N_2-Ar. The etching rate largely depends on the applied bias as seen in Fig. 7. The negative bias makes the etching rate of the films decrease, in contrast to the positive bias. This result indicates that the control of energy of ion species is very important to obtain the films with higher quality.

The oxidation of Si surfaces at 600°C using microwave-excited O_2-N_2 (or O_2-N_2-Ar) have been performed. In the low temperature oxidation the addition of N_2 was found to be very effective for the increase in the oxidation rate. The existance of NO species was identified by mass analysis. This indicates that the number of oxigen atoms in the reactant species is much enhanced through the reaction which produces the intermediate product as NO species. Figure 8 shows a C-V characteristic of the MOS diode at 1 MHz and the surface state density estimated by the Terman's method.

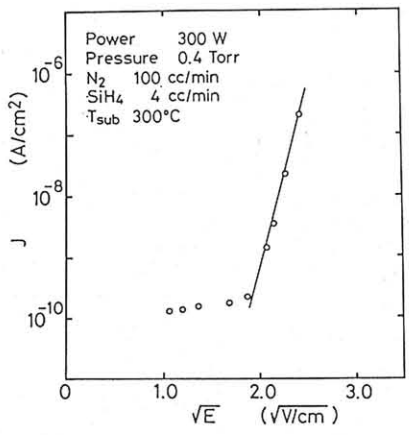

Fig.5 A typical I-V characteristic of SiN_x films.

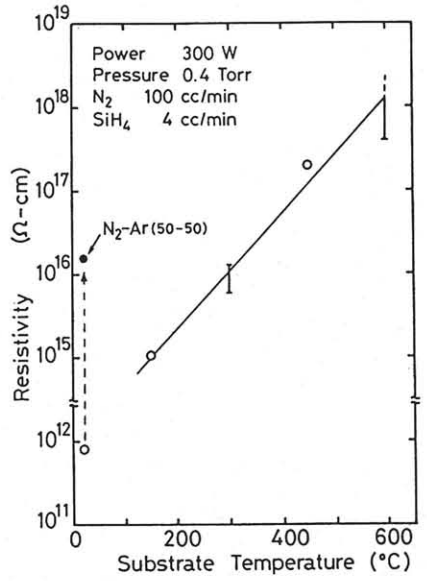

Fig.6 Resistivity of SiN_x films as a function of substrate temperature.

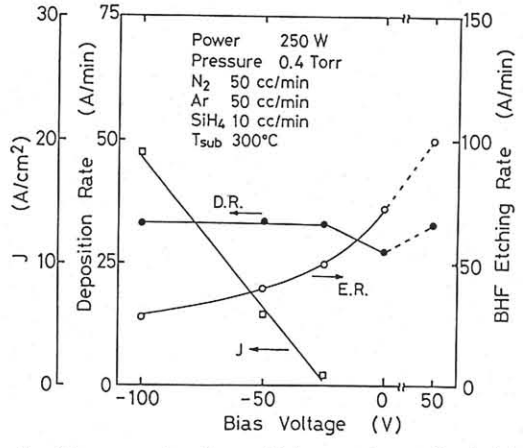

Fig.7 Changes in deposition rate and etching rate for SiN_x films and in substrate current density as a function of substrate bias voltage.

The result in Fig. 8 is of the as-grown sample without annealing in an H_2 ambient. It should be noted that the interface state density is as low as those for thermal oxidation and that no hysteresis is observed. In the RF-excited PECVD, the value of interface state density has been reported to be more than one order of magnitude higher than this value.[1),10)] Moreover, it has been reported that elimination of charged particles is effective for improving the Si-SiO_2 interface property,[1),11)] and that the bombardment of ions with the energy of 20-30 eV gives little damage to the substrate surface in the deposition method using an electron cyclotron resonance plasma.[12)] Therefore, the result in Fig. 8 shows that the substrates are little subject to the damage.

4. Conclusioin

SiN_x and SiO_2 films grown at low temperatures by using microwave-excited plasma have excellent properties as dielectric films. The composition of SiN_x films is independent of deposition conditions such as the gas flow ratio, the substrate temperature and the microwave power. The SiN_x films have a high resistivity and breakdown strength and have a low etching rate. The SiO_2 films grown by oxidation of silicon surfaces at 600°C have sufficiently high quality for use as a gate oxide. The Si-SiO_2 interface state density is as low as that for thermal oxides.

It can be concluded from the results in the present work that this method is very useful to VLSI technology.

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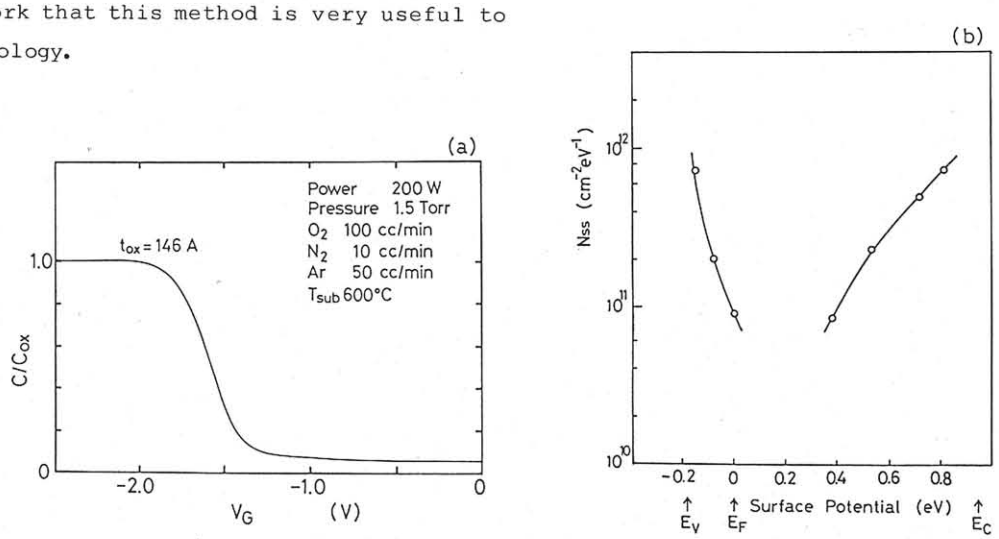

Fig.8 (a) C-V characteristic of MOSdiode at 1 MHz.
(b) Interface state density.