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Low Temperature SiO_2 Film Formation by Microwave Plasma Assisted Reactive Beam Deposition

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A system has been newly developed which can simultaneously perform Si evaporation and microwave oxygen plasma irradiation. High quality SiO_2 film having a dense structure (P-etch rate=6A/sec) can be formed without the need for both heating and an external substrate bias. Good SiO_2/Si interface properties were achieved (Dit=$2x10^{11}cm^{-2}ev^{-1}$) with and without direct plasma exposure of the Si substrate. Direct plasma exposure appears to be useful for film densification, and results in little radiation damage to the specimen.

1. INTRODUCTION

Low temperature dielectric film formation techniques, most notably plasma CVD (P-CVD)[1], are considered to have an important role to play in the development of future semiconductor devices. However there are several disadvantages to the P-CVD method. Examples are that films fabricated with this method suffer from radiation damage, a large amount of hydrogen cause hot carrier problem, and that the fabricated films have less density than thermal oxide.

In order to reduce radiation damage, several attempts to separate the specimen from plasma have been reported[2,3]. On the other hand, certain works on plasma oxidation[4,5] and P-CVD[6] have clarified that microwave plasma utilizing electron cyclotron resonance (ECR) means that little damage to the specimen will result. Densification of the film has also been achieved through microwave (ECR) P-CVD[7].

We have applied such use of microwave plasma to a Si vapor-oxygen plasma direct reaction methodology which has been known as activated reactive evaporation (ARE)[8] and recently modified by Chang et al.[9] This method can reduce the hydrogen content in the formed films, since high-purity Si vapor is used instead of gases containing hydrogen, such as SiH_4.

In this report, we will explain the details of this microwave plasma assisted reactive beam deposition (MP-RBD) method, and report on the properties of the formed SiO_2 film. The effects of plasma exposure on film formation and film properties will also be discussed.

2. MP-RBD SYSTEM AND EXPERIMENT

A schematic view of the MP-RBD system is shown in Fig. 1. It is composed of a microwave plasma source, electron beam evaporation source (E-gun), and vacuum chamber where a specimen is to be loaded. Dual beams of Si and oxygen plasma simultaneously irradiate the substrate, and a reaction between evaporated Si and excited oxygen taking place on the substrate leads to formation of SiO_2 film. Because of the geometry of the equipment, each beam's angle of incidence to the substrate surface is about 45^o.

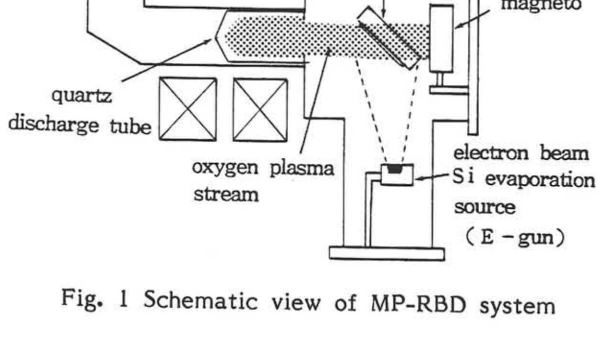

Fig. 1 Schematic view of MP-RBD system

This system is similar to one first proposed by Chang et al.[9] involving the use of a RF (Radio Frequency) plasma source. However we found microwave plasma to be more suitable for at following reasons. Since microwave plasma can be ignited easily even at pressures of the order of 10^{-2}Pa, an E-gun can be operated simultaneously to evaporate Si. Moreover the existence of the axial magnetic field results in the advantage that the plasma stream is confined radially and transported to the specimen along the field line. Therefore, the plasma can be separated from the E-gun and chamber wall. This is helpful both in avoiding E-gun breakdowns in a plasma ambience, and in avoiding possible contamination of specimens resulting from chamber wall sputtering.

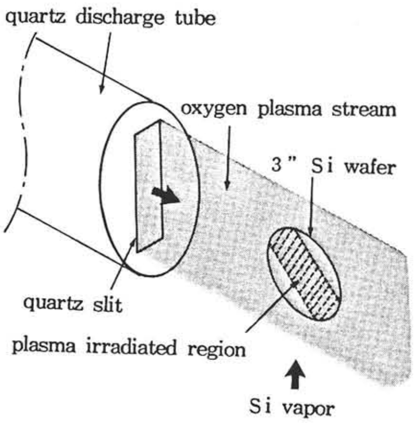

Fig. 2 Conceptual representation of plasma irradiation

In order to investigate actual effects of plasma exposure, a limited region on 3 inches wafers was irradiated by setting a quartz slit (30mmx80mm) at the exit of the quartz discharge tube (100mm in diameter), as shown in Fig. 2.

Deposition conditions for the SiO_2 film were as follows. Oxygen pressure was $2\text{-}6\times10^{-2}$Pa, and microwave power was 100W. The Si substrate was kept floating electrically, and was not heated. The deposition rate was about 1nm/min. In addition, film formation using Si evaporation in O_2 gas (2×10^{-2}Pa) was also carried out for comparison.

To evaluate the film properties, ellipsometry, IR absorption, and a P(Pliskin)-etch were used. Hydrogen content could be roughly estimated from IR absorption. In addition, variations in IR absorption characteristics under high-temperature N_2 anneals (600°C, 1h and 1000°C, 1h) were also examined. Capacitance-voltage (C-V) measurements by an MOS capacitor were performed to characterize the SiO_2/Si interface and examine radiation damage.

3. RESULTS AND DISCUSSION

3.1.SiO_2 film formation and film properties

The film thickness of the plasma irradiated region was 30-40% less than that of the non-irradiated region. This result contrasts with results from microwave (ECR) P-CVD, where growth of the film is restricted to the plasma irradiated region. Although the mechanism of this effect has yet been clarified, it can be said that physical sputtering of SiO2 film by ions is practically impossible. Because the plasma sheath voltage is 10-20ev under non-biased conditions, ion energy is insufficient to sputter SiO_2 film. On the other hand, chemical etching of SiO_2 by Si[10] or reduction of Si sticking probability seem to be possible mechanisms under plasma direct irradiation conditions.

Refractive index measurements of the film were in the range of 1.47-1.50 under conditions described above. An increased Si deposition rate makes this values rise above 1.5, thus implying Si-rich film formation. Under conditions in which stoichiometric film was formed, O_2 flux was estimated to be three orders greater than Si flux, and ion (O_2^+) flux was estimated to be one order greater.

The IR absorption spectrum for MP-RBD SiO_2 film (plasma irradiated) is shown in Fig. 3, where a comparison is made with the case for thermal oxide and a film made by Si evaporation in O_2 gas ambience (Si(in O_2)film). Three absorption bands

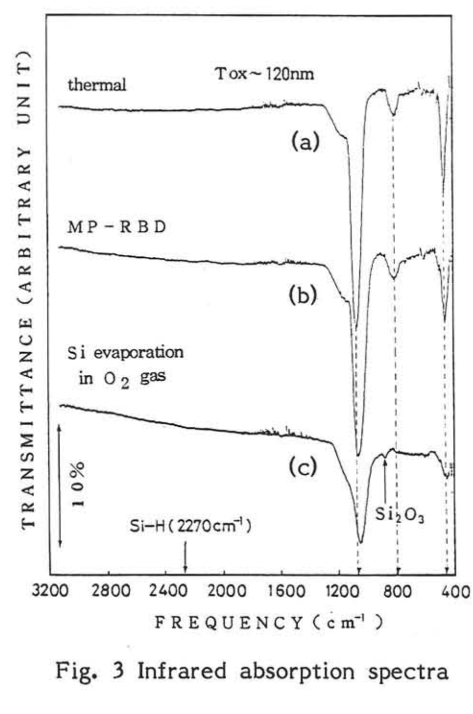

Fig. 3 Infrared absorption spectra

characteristically observed in SiO_2 are clearly seen in the spectrum of the MP-RBD film (b) as well as thermal oxide (a). On the other hand, Si(in O_2) film spectrum (c) shows two different features. Namely, at $800cm^{-1}$, hardly any Si-O bending mode absorption is observed, while a Si_2O_3 absorption peak appears at $880cm^{-1}$[11]. In addition, the Si-H band ($2270cm^{-1}$) is not appreciable, which shows that these films do not contain a considerable amount of hydrogen.

Figure 4 shows variation in IR absorption spectra with high temperature annealing in N_2 gas. An increase in Si-O stretching mode absorption ($1080cm^{-1}$), a shift in peak position, and a narrowing of this mode are all observed after annealing. It is more remarkable for the Si(in O_2) film, which indicates the existence of a large amount of unreacted oxygen. The Si_2O_3 peak also disappeared, and a Si-O bending mode appeared. After 1000°C annealing for one hour, the MP-RBD film spectrum became equivalent to that for thermal oxide. However, the Si(in O_2) film spectrum still showed a smaller absorption peak than that for thermal oxide when the thickness was the same. The results clearly show that Si-O bond formation is enhanced by use of oxygen plasma.

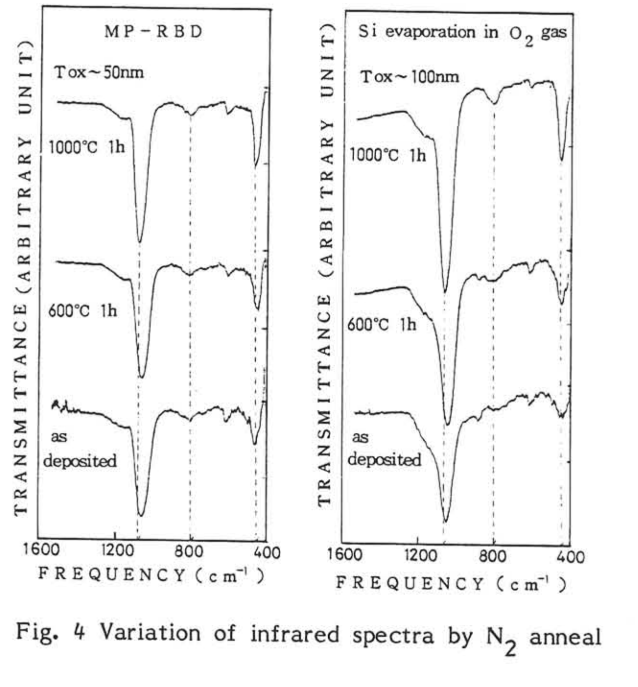

Fig. 4 Variation of infrared spectra by N_2 anneal

The P-etch rate of MP-RBD film in the plasma irradiated region was about 6A/sec. This is three times greater than the rate for thermal oxide, but only one-fourth that of conventional P-CVD films. In the non-irradiated region, the rate was almost two times greater. Si(in O_2) film has a P-etch rate of more than 100A/sec. Therefore, ion bombardment at moderate energies (10-20ev) appears to be one reason densified film is obtained. Another possibility is the enhanced Si-O reaction which is limited to the substrate surface by utilizing low pressure plasma.

3.2. SiO_2/Si interface properties

The C-V characteristics of an MOS capacitor are shown in Fig. 5. The SiO_2/Si interface trap level density (Dit) was calculated using high frequency and quasi-static C-V measurement (Fig. 6). After post-metallization annealing (H_2, 450°C, 30min), Dit became $1.85x10^{11}cm^{-2}eV^{-1}$ at the mid gap. No remarkable difference was found between irradiated and non-irradiated regions.

This value is about one order greater than that for thermal oxide, and nearly the same value is achieved by indirect P-CVD.[2,3] However, it has been reported that direct exposure of a specimen to RF plasma increases Dit to where it becomes more than one order of magnitude higher than this value.[2]

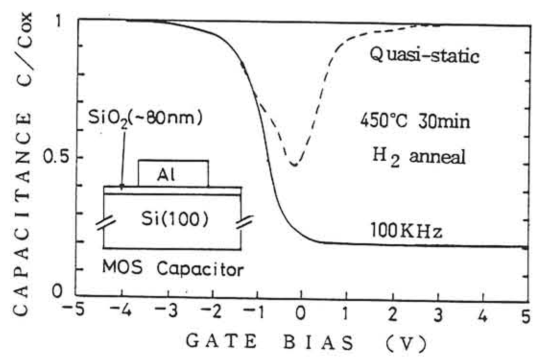

Fig. 5 C-V characteristics of MOS capacitor

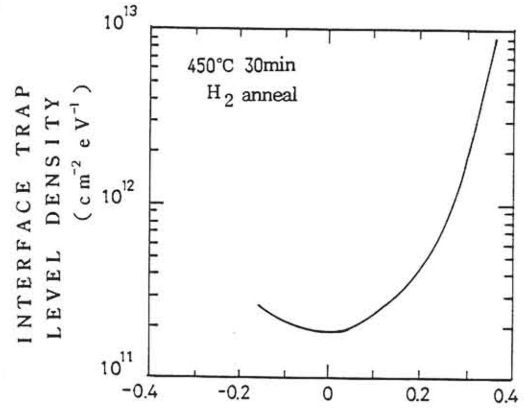

Fig. 6 Trap level density of SiO_2/Si interface

Furthermore in ARE with RF plasma, charged particle elimination through use of a magnetic field has been found to be effective for improving SiO_2/Si interface property[9]. Therefore this result shows that the microwave plasma gives little damage to the specimen.

Energy analysis of the microwave ion source[12] leads to the conclusion that the plasma potential and ion energy spread are lower for microwave or ECR plasma than for RF plasma. This is probably the reason for the damage free nature of the present plasma source.

4. CONCLUSIONS

Microwave plasma assisted reactive beam deposition (MP-RBD) system was newly developed by combining a microwave plasma source and electron beam evaporation source. Using it, high quality SiO_2 film could be obtained without heating or applying bias to the substrate. Si-O bond formation was enhanced using oxygen plasma, and a film structure similar to that of thermal oxide was realized. The P-etch rate of the film was about 6A/sec, which is three times greater than that of thermal oxide. Plasma exposure was seen to be effective for film densification. In addition the SiO_2/Si interface trap level density Dit is about $2x10^{11}cm^{-2}eV^{-1}$. This value is independent of whether plasma is irradiated directly or not.

In conclusion, direct plasma exposure appears to be good for film properties when the system described here is employed.

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