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Silicon Nitride Thin Films Prepared by ECR Plasma CVD

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Silicon nitride thin films prepared by ECR plasma CVD exhibited excellent physical and electrical properties. The refractive indices of the films were 1.9-2.0. The etch rate was extremely as low as 0.5nm/min. The resistivity and breakdown voltage were $>10^{17}\Omega$ cm and > 10MV/cm, respectively. The interface state density of between silicon nitride and silicon was $1\text{-}5\times10^{11}$ /cm^2 /eV. The optical emission spectroscopy has been measured during the deposition.

1. Introduction

Silicon nitride (SiN) thin films play an important role as passivation films in semiconductor devices. For formation of SiN films, chemical vapor deposition (CVD), in particular, the plasma CVD has been mainly used(1). The plasma CVD method has an advantage of low substrate temperature, however, the method has a disadvantage of degradation caused by hydrogen contamination of source materials such as silane (SiH_4) and ammonia (NH_3). Pure nitrogen (N_2) has been used in place of NH_3 to eliminate the hydrogen contamination, however, the film quality is insufficient comparing to films prepared with NH_3. It has been considered that the nitrogen is not sufficiently activated.

Recently electron-cyclotron-resonance (ECR) plasma CVD has been developed (2),(3) and become attractive as a method of SiN film formation due to the possibility of minimizing the above-mentioned problems and further lowering of substrate temperature.

In this paper we studied the effect of N_2 partial pressure in ECR plasma CVD , measured physical and electrical properties of the SiN films, and compare the results with those of conventional methods. In addition, we report a result of optical emission spectroscopy during the deposition.

2. Experimental

The ECR plasma CVD apparatus used for the deposition of SiN films is schematically shown in Fig.1. The apparatus consists of a plasma chamber and a reaction chamber. The plasma chamber is attached to a 2.45GHz microwave source and surrounded with coils which generate a magnetic field of 0.0875T for ECR condition.

For the deposition, N_2 gas and SiH_4 gas (100% SiH_4) were introduced into the plasma chamber and the reaction chamber, respectively. The nitrogen plasma generated in the plasma chamber flows into the reaction chamber, where decomposition and reaction occur resulting the deposition of SiN thin films on the substrate.

The substrate temperature was not intentionally elevated and not exceeded 60°C during the deposition. The SiH_4 partial pressure was kept at 6.5×10^{-3} Pa and the N_2 partial pressure (P_{N2}) was varied from 6.5×10^{-3} to 6.5×10^{-2} Pa. Silicon wafers (p-type, 25Ωcm) with (100) orientation were used as substrates.

Physical properties of the deposited films were evaluated with refractive index, etch rate and infrared (IR) absorption spectra. Electrical properties of films were measured with current-voltage (I-V) and capacitance-voltage (C-V) characteristics. The refractive indices were determined by the ellipsometry.

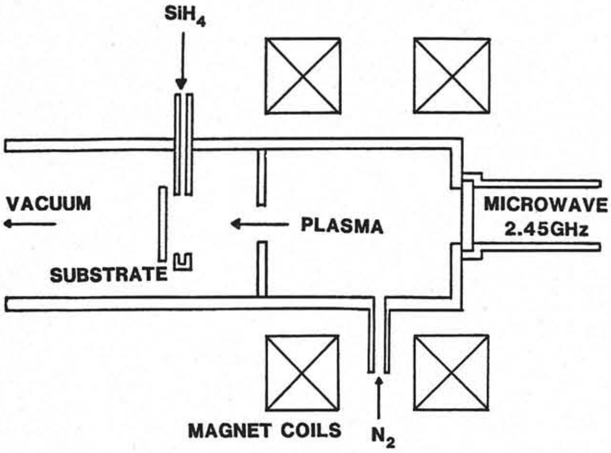

Fig. 1 The ECR plasma CVD apparatus.

Etch rates were measured using a buffered HF (BHF) solution. The measurement of I-V characteristics of films was carried out for a metal-SiN-metal (MNM) structure with Al electrodes 100nm thick. The SiN used was deposited at P_{N2} =$3.3x10^{-2}$Pa and 100nm thick. For the measurement of the C-V chacteristics to evaluate the interface properties between silicon and SiN, an SiN film about 130nm thick was deposited on a silicon substrate at P_{N2}=$3.3x10^{2}$Pa followed by a deposition of an Al electrode to make a metal-SiN-silicon (MNS) structure.

3 Results and Discussion

3.1 Physical properties

Figure 2 shows the deposition rate, refractive index and etch rate of the films as functions of P_{N2}. The deposition rate was 11nm/min and independent of P_{N2}. The deposition rate was limited by SiH_4 partial pressure under the present condition. The refractive indices were 1.9-2.0, which were comparable to those of conventional thermal CVD films. It is found that the refractive index is related to the flow ratio, N_2/SiH_4. The optimum flow ratio in ECR plasma CVD is 1-5. These value are remarkably smaller than those of conventional plasma CVD methods(10-100)(4). This fact indicates that N_2 is sufficiently activated in ECR plasma.

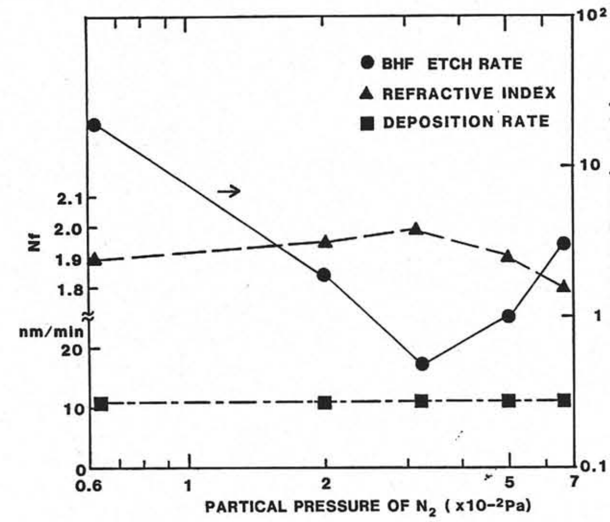

Fig. 2 The deposition rate, the refractive index and the etch rate as functions of PN2.

The etch rate in a buffered HF (BHF) solution (50% HF:40% NH_4F=3:17, 20°C) exhibited a minimum value of 0.5 nm/min at N_2 partial pressure of $3.3x10^{-2}$Pa. This minimum etch rate is comparable to those for thermal CVD films (5). It has known that the bonds of Si-N, Si-H, N-H and Si-O strongly influence the etch rate (6). It is considered that there exist much less Si-H bonds of the films prepared by ECR plasma CVD comparing the conventional plasma CVD methods.

3.2 Infrared (IR) absorption spectra

Figure 3 shows IR absorption spectra of the films for P_{N2}=$6.5x10^{-3}$ and $2x10^{-2}$ Pa. For P_{N2}=$2x10^{-2}$ Pa the Si-N bond and N-H bond were clearly observed, while the Si-H bond was scarcely observed. For P_{N2}=$6.5x10^{-3}$ Pa the Si-H bond was clearly observed in addition to the Si-N and N-H bonds. At above P_{N2}=$2x10^{-2}$ Pa IR absorption spectra did not varied. It is considered that the existence of the Si-H bond degrades extremely the etch rate chacteristics of the SiN films. In the conventional plasma the Si-H bond has been clearly observed(4,6).

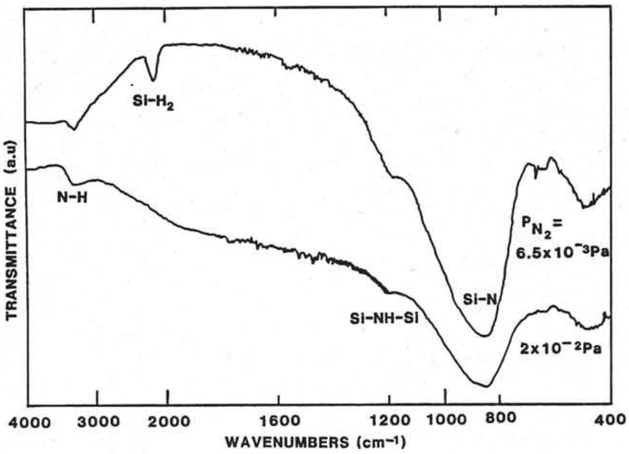

Fig. 3 IR absorption spectra of the films for P_{N2}=6.5x10^{-3}, 2x10^{-2} Pa.

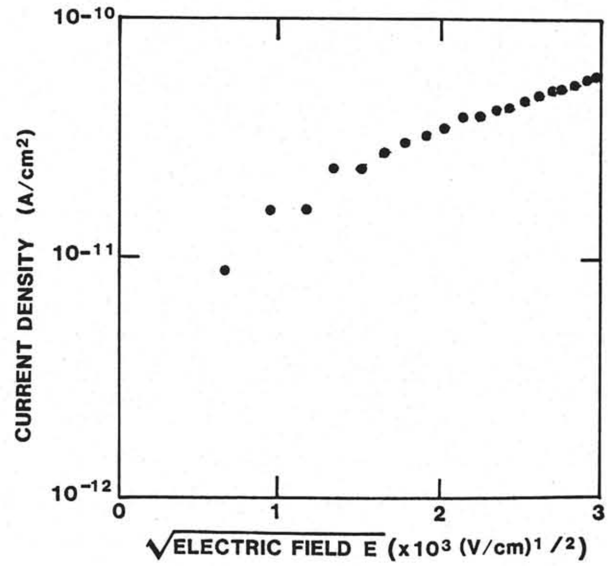

Fig. 4 log(I) - $V^{1/2}$ characteristics of the film for P_{N2}=3.3x10^{-2}Pa.

3.3 Current-Voltage (I-V) characteristics

Figure 4 illustrates a log (I) - $V^{1/2}$ behavior of SiN in the MNM structure. The resistivity of the film was >10^{17}Ω cm and much larger than that of thermal CVD or conventional rf-plasma CVD SiN films(4,7,8). The breakdown voltage of this film was larger than 10MV/cm, which was comparable with the thermal CVD(7). It is considered that both the gap states and the tail states in films prepared by the ECR plasma CVD scarcely exist and the defect concentration is low.

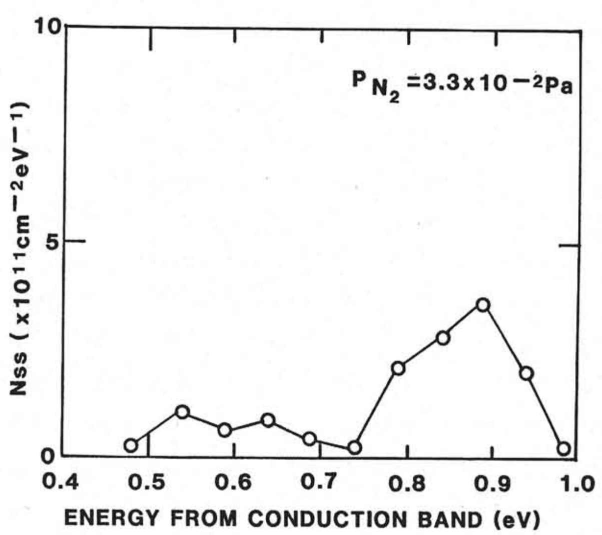

Fig. 5 The interface state density N_{ss} at high frequency (1MHz) C-V chacteristics of the film for P_{N2}=3.3x10^{-2}Pa.

3.4 Capacitance-Voltage (C-V) chacteristics

The energy distribution of the interface state density N_{ss} at high frequency (1MHz) C-V chacteristics of the MNS structure is shown in Fig.5. The flat band shift voltage V_{FB} was -0.4V except for the potential difference between Al and Si. This indicates that the positive charge exists at the interface between Si and SiN. The N_{ss} exhibited a maximum value and 5x10^{11} $cm^{-2}eV^{-1}$ at around 0.9 eV below the conduction band. This value of N_{ss} is comparable with those of the conventional plasma CVD films(7,8).

3.5 Optical Emission Spectroscopy

A typical optical emission spectrum during the deposition is shown in Fig.6. In the SiH_4-N_2 ECR plasma we can detect many emission species such as the Si, H , N_2 and N_2^+.

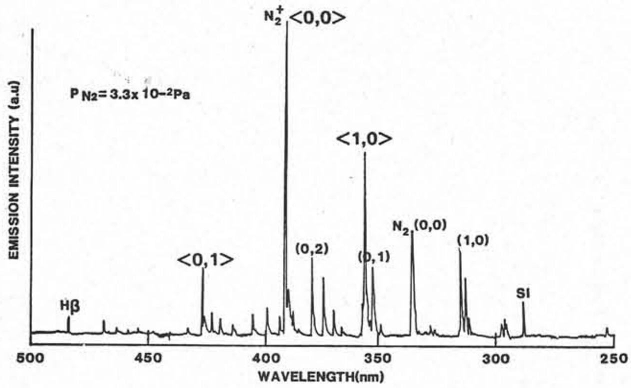

Fig. 6 A typical optical emission spectrum during the deposition in SiH_4 and N_2 ECR plasma.

The emission of nitrogen molecules (337nm, N_2 (0,0)), nitrogen ions (392nm, N_2^+(0,0)), Si atom (288nm, UV43) and hydrogen atom (486nm, Hβ) were observed. The emission intensity of N_2^+(0,0) is remarkably strong and comparable to that of N_2(0,0) . The emission lines expected from excited nitrogen atoms (411, 415 nm) could not be detected. The other emission species, i.e., SiH(414nm), NH, Hα and H_2 were hardly observed, partly because the emission intensities of those species are weaker than those of N_2 and N_2^+. In conventional plasma CVD methods the emission of N_2^+ was hardly observed. Therefore, it is found that N_2 in ECR plasma is much activated in comparison with conventional rf plasma(9). In conventional rf plasma the emission intensity of SiH was stronger than those of Si and Hβ(10). SiH_4 in ECR plasma may hence be decomposed sufficiently into Si and H atoms.

4. Conclusion

We have successfully prepared SiN films by ECR plasma CVD at substrate temperature lower than 60°C. The minimum BHF etching rate, 0.5 nm/min was obtained. The refractive indices of films are 1.9-2.0. These physical properties were much better than those of conventional plasma CVD and almost comparable with the best values of the thermal (high temperature) CVD. The resistivity and breakdown voltage were $>10^{17}\Omega$ cm and >10MV/cm, respectively.

As a result of the optical emission spectroscopy, the emission intensities of N_2^+, Si and H in SiH_4+N_2 ECR plasma were stronger than those of plasma conventional CVD. It is considered that N_2 is much activated and SiH_4 are decomposed sufficiently into Si and H atoms in ECR plasma.

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6. References

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