Extended Abstracts of the 17th Conference on Solid State Devices and Materials, Tokyo, 1985, pp. 287-290

Deposition and Properties of Silicon Nitride Film by Si_2F_6-N_2-H_2 Glow Discharge

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Deposition and properties of silicon nitride (SiN) films, prepared by Si_2F_6-N_2-H_2 gas glow discharge, were studied, and the potentiality in applying this SiN film to silicon devices was investigated in detail. Deposition rate of the SiN film is as high as 200-300 Å/min under typical conditions. The SiN film has a considerable amount of fluorine atom, and hydrogen within the film is tightly bonded to nitrogen atom. It was also clarified that silicon devices covered with the SiN film shows no degradation related to hydrogen.

1. Introduction

Plasma CVD silicon nitride (SiN) film has been widely used as a passivation film for VLSI[1]. However, SiN film, which is deposited by SiH_4-NH_3 gas glow discharge, causes device reliability degradations due to hydrogen, such as enhancement of MOS transistor threshold voltage shift during stressing[2] and variation in poly-silicon resistor resistivity[3].

Recently, it has been reported that plasma deposition by utilizing SiF_4 gas based reactant gas glow discharge[4], although its deposition rate is low, forms SiN film containing F atom (F-SiN film), with a smaller amount of hydrogen than SiN film prepared by SiH_4-NH_3 glow discharge.

This paper presents a F-SiN film deposition method with high deposition rate by utilizing Si_2F_6 gas, which is more chemically active than SiF_4. It also clarifies potentiality to apply this film to silicon devices, as a result of studying chemical and electrical properties of the F-SiN film.

2. Experimental

2-1 Film Deposition

A parallel plate type plasma reactor with 13.56 MHz discharge frequency was used to deposit all the SiN film.

F-SiN films were deposited employing Si_2F_6-N_2-H_2 gas mixture, where $Si_2F_6/(N_2+H_2)$ gas flow rate ratio was varied from 0.025 to 0.06 and $H_2/(Si_2F_6+N_2)$ gas flow rate ratio was also varied from 0.2 to 2. Substrate temperature was 390°C.

SiN film, which was used as a reference film, was deposited at 390°C substrate temperature employing conventional SiH_4-NH_3 gas mixture.

2-2 Film Properties

Infrared spectra, Auger spectra, refractive index, etching rate in buffered HF solution and film stress were measured on the F-SiN film deposited on Si wafer, to investigate structural or chemical properties.

Electrical characteristics, such as leakage current through the film and surface charge density, were measured on an MIS diode structure of Al/100nm thick SiN film/P-Si.

2-3 Application

In order to clarify the influence of the film on device characteristics, n-MOSFET with Leff= 1.8 µm and poly-silicon resistor, which were covered with the SiN film, were fabricated. Then, the n-MOSFET was annealed at 450°C in N_2 for 10 minutes, and threshold voltage shift was measured under DC bias stress. The poly-silicon resistor was annealed at 450°C in N_2 for 10-60 minutes, and resistivity was measured as a function of annealing time.

Further, thermal crack generation for the F-SiN film and Al hillock growth were investigated using a layered structure of 0.5 µm thick SiN film/ 1µm thick Al film / CVD SiO_2, applying the thermal stress at 450°C in N_2 for 60 minutes.

3. Results and Discussions

3-1 Film Deposition

The deposition rate as a function of $H_2/(Si_2F_6+N_2)$ gas flow rate ratio, where (Si_2F_6 $+N_2$) gas flow rate is kept constant, is shown in Fig.1. The film can be deposited, even when there is no hydrogen reactant gas, with rather high deposition rate of 190 Å/min. However, film, prepared with no hydrogen gas, reacts with H_2O in air at room temperature to change into SiON film. On the other hand, films deposited by using the hydrogen gas are chemically stable. Therefore, the hydrogen reactant gas is needed to deposit chemically stable F-SiN film.

The deposition rate as a function of $Si_2F_6/(N_2+H_2)$ gas flow rate ratio, where (N_2+H_2) flow rate is kept constant, is shown in Fig.2. The deposition rate is found to increase with increasing Si_2F_6 gas flow rate. At maximum of Si_2F_6 flow rate in this experiment, the deposition rate, which is as high as 320 Å/min, is obtained. This high deposition rate indicates that the glow discharge method utilizing Si_2F_6 based reactant gas mixture is acceptable to real productions.

3-2 Chemical or Structural Properties

Infrared absorption spectrum for the 100nm thick F-SiN film, deposited at gas flow rate ratio of $H_2/(Si_2F_6+N_2)=1.22$, is shown in Fig.3, in comparison with that for reference SiN film. Two distinctive absorption peaks are observed for the F-SiN film. The peak at 920cm^{-1} is due to Si-N bond absorption and the peak at 3375 cm^{-1} is due to N-H bond absorption. However, no absorption corresponding to Si-H bond was observed. On the other hand, there are three absorption peaks at 880, 2175 and 3337 cm^{-1}, corresponding to Si-N, Si-H and N-H bonds, respectively, for the reference film. The N-H absorption peak position for the F-SiN film is at a higher wavenumber compared with that for the reference film, indicating that hydrogen atom in the F-SiN film is more tightly bonded to nitrogen atom, compared with the reference film. It is due to the existence of F atoms(5).

Refractive index, F/Si and N/Si atomic ratios, and hydrogen concentration are shown in Fig.4, as a function of $H_2/(Si_2F_6+N_2)$ flow rate ratio. The refractive index slightly increases with increment of H_2. The N/Si atomic ratio increases with increace in H_2 flow rate, while the F/Si atomic ratio decreases. The hydrogen concentration is independent from H_2 gas flow rate. Its value is $7x10^{21}cm^{-3}$, which is less than that for the reference SiN film($3x10^{22}$ cm^{-3}).

Etching rate in buffered HF solution and film stress are also shown in Fig.5, as a function of $H_2/(Si_2F_6+N_2)$ gas flow rate ratio. The etching rate for the F-SiN film decreases from 200Å/sec to 100Å/sec with increasing H_2 gas flow rate, and is about one order of magnitude larger than that for the reference film, 10A/sec. The film deposited at low H_2 gas flow rate shows compressive stress($2x10^9$ dyn/cm^2), while the film deposited at high H_2 gas flow rate shows tensile stress($2x10^9$ dyn/cm^2), which is less than that for the reference film (tensile stress, $4x10^9$ dyn/cm^2).

Figure 6 shows hydrogen concentration in the film, when subjected to thermal annealing in N_2 for 30 minutes at 500 or 650°C, for the F-SiN and the reference SiN film. After annealing, the hydrogen within the reference SiN film is evolved, while no hydrogen evolution was observed for the F-SiN film. These results also indicate that hydrogen in the F-SiN film is tightly bonded to N atom .

3-3 Electrical Properties

Surface charge density, which was evaluated from flat band voltage of capacitance-voltage characteristics,and leakage current at 1MV/cm electrical field are shown in Fig.7,as a function of H_2 gas flow rate. It is shown that net positive charges are present in the F-SiN film, as observed for the reference film, and the surface charge density decreases from $1.25x10^{12}$ cm^{-2} to $6x10^{11}$ cm^{-2} with increasing H_2 gas flow rate. Leakage current also decreases with increace of H_2 gas flow rate, and the current density($8x10^{-9}$ A/cm^2) at maximum H_2 gas flow rate is smaller than that ($4x10^{-8}$ A/cm^2) for the reference SiN film. As a whole, electrical properties for the F-SiN film is similar to those for the reference SiN film, as far as the properties studied here are concerned.

3-4 Application to Silicon Devices

The F-SiN film has been applied to Si-gate n-MOSFET and poly-silicon resistor as a final passivation film. Then, the poly-silicon resistor was annealed at 450°C in N_2 for 10-60 minutes. The n-MOSFET was annealed at 450°C in N_2 for 10 minutes, and was exposed to DC bias stress for 100-4500 sec.

Figure 8 shows the resistivity variation for the F-SiN film covered poly-silicon resistor, as a function of annealing time duration,together with that for the reference SiN covered poly-silicon resistor. The resistivity of reference SiN film covered poly-silicon resistor decreases with increase in annealing time. On the other hand, the resistivity for F-SiN film covered poly-silicon resistor shows no variation even after 60 minute annealing.

Figure 9 shows the dependence of threshold voltage shift on the stress time for the F-SiN film covered n-MOSFET, in comparison with the results for reference SiN film covered and for no film covered n-MOSFETs. The reference SiN film covered FET shows large threshold voltage shift. On the other hand, for the F-SiN film covered FET, the shift is very small, and is nearly equal to that for no film covered one.

These results obtained for the poly-silicon resistor and the n-MOSFET suggest that hydrogen related device degradations are very small for the F-SiN film covered devices.

Further, thermal crack generation in the F-SiN film and hillock formation at the surface of aluminum covered with the F-SiN film have been investigated. It has been clarified that the crack is not generated even after annealing at 450 C for 60 minutes, in the F-SiN film, and that the F-SiN film has the effect to suppress aluminum hillock formation during film deposition processing.

4 Conclusion

Deposition and properties of silicon nitride (SiN) films, prepared by Si_2F_6-N_2-H_2 gas glow discharge, were studied, and the potentiality to apply this SiN film to silicon devices was investigated in detail.

Deposition rate is as high as 200-300 A/min under typical conditions, indicating that the glow discharge method utilizing Si_2F_6 based reactant gas mixture is acceptable to real productions.

The deposited SiN film has a considerable amount of fluorine atom, and hydrogen within the film is tighly bonded to nitrogen atom. Leakage current through the film is as small as 8×10^{-9} A/cm^2 at 1 MV/cm.

It was also clarified that silicon devices covered with this SiN film shows no degradation related to hydrogen.

Results obtained in this work indicate that the SiN film, prepared by Si_2F_6-N_2-H_2 gas glow discharge, is very promising for VLSI device productions.

Acknowledgement

The authors would like to acknowledge Drs. H. Muta and T. Yanagawa for their helpful suggestions and encouragement, and Mr. Takagi and Dr. Konuma of ANELVA Co. for their help with the experiment.

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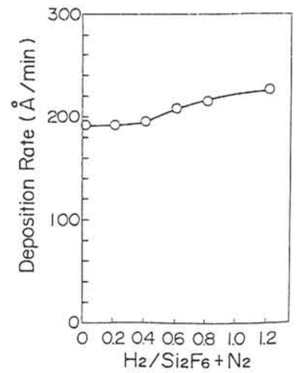

Fig.1 F-SiN film growth rate as a function of $H_2/(Si_2F_6+N_2)$ gas flow rate ratio.

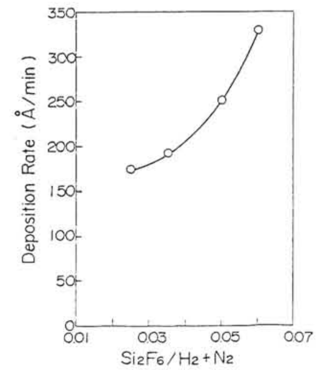

Fig.2 F-SiN film growth rate as a function of $Si_2F_6/(N_2+H_2)$ gas flow rate ratio.

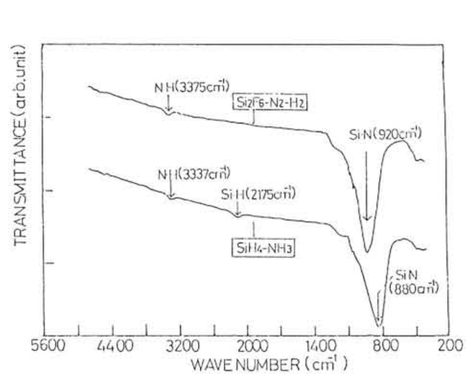

Fig.3 FTIR spectrum for SiN film by Si_2F_6-N_2-H_2 glow discharge, in comparison with that for SiN film by SiH_4-NH_3 glow discharge.

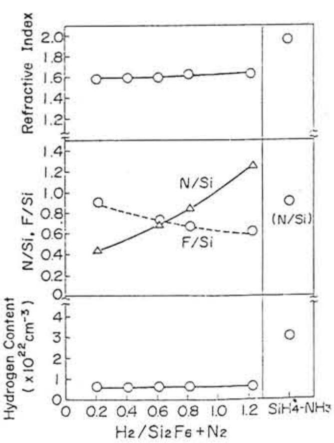

Fig.4 Refractive index, N/Si F/Si atomic ratios and hydrogen concentration for F-SiN film as a function of $H_2/(Si_2F_6+N_2)$ gas flow rate ratio.

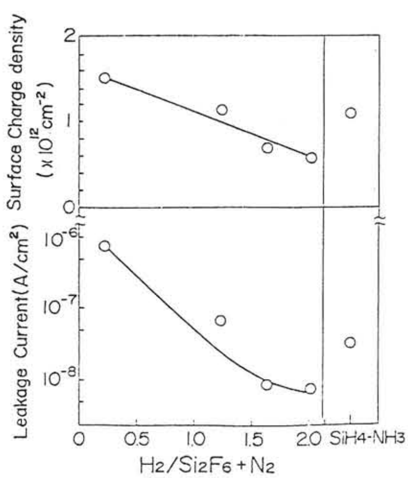

Fig.7 Leakage current at 1MV/cm and surface charge density, as a function of $H_2/(Si_2F_6+N_2)$ gas flow rate ratio, together with those for SiN film prepared by SiH_4-NH_3 glow discharge.

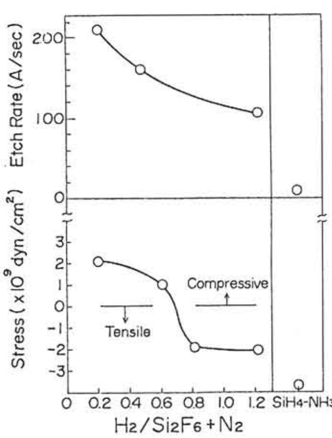

Fig.5 Etching rate in buffered HF solution and film stress for F-SiN film as a function of $H_2/(Si_2F_6+N_2)$gas flow rate ratio.

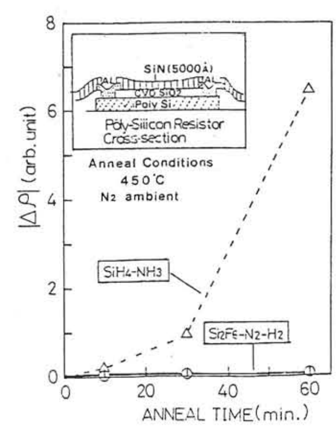

Fig.8 Poly-silicon resistor resistivity variation as a function of annealing time, at 450°C anneal temperature in N_2 ambient.

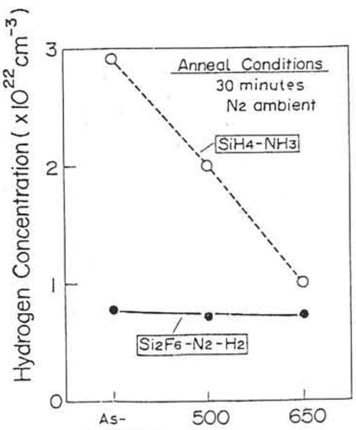

Fig.6 Anneal temperature dependences of hydrogen concentration within F-SiN films subjected to thermal annealing in N_2 for 30 minutes.

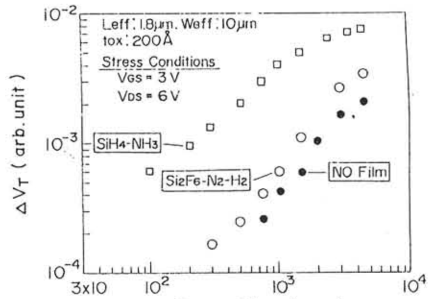

Fig.9 Dependence of threshold voltage shift under DC stress for Si-gate n-MOSFET on stress time.