NITRIDING OF SILICON WAFER IN A RADIOFREQUENCY DISCHARGE

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ABSTRACT

Nitriding of silicon wafer was carried out in a nitrogen or nitrogen-hydrogen plasma under a pressure of 10 Torr and 800°C. The nitriding succeeded by nitriding with nitrogen-hydrogen plasma. Reaction kinetics obeyed a general relationship, $X_0^2+AX_0 = B(t+\tau)$.

1. INTRODUCTION

Recentry very thin uniform silicon nitride films less than 100 A thickness have been obtained on silicon wafer by thermal reaction with nitrogen at ranging from 1200° to 1300°C (1). Thermal nitriding of silicon in ammonia or ammonia-argon mixture at temperature between 900° and 1200°C resulted in the formation of oxy-nitride film that was oxidation resistant (2). One of the authors (O.M.) studied nitridings of titanium (3), zirconium (4) and steel (5) by nitrogen or nitrogen-hydrogen plasma which were prepared with a radiofrequency discharge. Titanium and zirconium were nitridedat temperature between 800° and 900°C heated inductively and obtained TiN and ZrN films of 10 μm thickness. Steel was nitrided at temperature of 500° - 650°C by heating with electric furnace set appart from the inductive coil and Fe_4N film of 10 μm thickness was obtained. In this paper, the nitriding of silicon wafer is studied in the same way of the nitriding steel. The effect of the addition of hydrogen into nitrogen for nitriding silicon wafer is also discussed by means of plasma diagnostics, such as an emission and mass spectroscopies and an electrical double probe technique.

2. EXPERIMENTAL

Materials: Silicon p type (100) oriented CZ wafer with boron doping 400 m thickness were used as a starting material. Specimens 20x10 mm^2 cut from the wafers were chemically cleaned by degreasing, etching in HF solution (HF 1 : H_2O 9) and rinsing with deionized water. They were then dried in a vacuum desiccator. Purified nitrogen and hydrogen (both of 99.99999 % purity) were used as plasma gases without further purification.

Apparatus and Procedures: The nitriding apparatus is shown schematically in Fig. 1. The discharge tube was consisted of a quartz tube of 80 cm long and 18 mm in diameter. Radiofrequency power was applied from a 13.56 MHz, 500W generator and was transferred to the gas by means of an impedance matching network. A specimen was set in apart from the inductive coil and was heated at 800°C with an electric furnace. The total pressure was maintained under 10 Torr of nitrogen or nitrogen-hydrogen (4:1) plasma and an rf power was 300W. The plasma region extended about 40 cm long in the discharge tube and the specimen was covered with plasma. The plasma diagnostics were carried out by means of emission spectroscopy, mass spectroscopy and electri double probe technique. After nitriding for desired time, both film thickness and refrective index were measured by an elipsometric technique. The products were identified by means of infrared spectroscopy and electron diffraction.

3. RESULTS AND DISCUSSION

Measurement of Film Thickness and Refrective Index: When the silicon wafer was set in the discharge tube and reacted with nitrogen plasma for desired time up to 8 hours, no nitriding was observed and SiO_2 was formed. The film thickness formed on the silicon wafer was fluctuated between 60A - 500A and the refrective index was 1.5 - 1.6. When the silicon wafer was reacted with nitrogen-hydrogen plasma for desired time, nitriding was succeeded. The film thickness and refrective index of nitrided silicon wafer are listed in Table 1. For products obtained by nitriding with nitrogen-hydrogen plasma for longer than 1 hour, the refrective index was 2.0 ± 0.1 and it was comparable with that of silicon nitride obtained by CVD. The refrective index of the product obtained by nitriding with nitrogen-hydrogen plasma for 30 min was 1.77. It was comparable with that of silicon oxynitride (6).

Kinetic Study: The relationship between the film thickness and the nitriding time is shown in Fig. 2. The line bent at nitriding time of 2 hours. Deal et al. showed that the silicon oxidation kinetics is represented in a general relationship as eq. 1 (7).

$$x_0^2 + Ax_0 = B(t + \tau) \qquad (1)$$

where x_0 is oxide film thickness, t oxidation time, A, B a constant, τ a shift of time coordinate. Two limitting forms are driven from eq. 1. At relatively large time i.e. $t > A^2/4B$ and also t, parabolic oxidation law, $x_0^2 = Bt$, is obtained. For relatively small time i.e. $t < A^2/4B$, linear oxidation law, $x_0 = B/A(t + \tau)$ is obtained. In nitriding silicon wafer, the kinetics is represented by linear law up to 2 hours, then the kinetics is represented by parabolic law. The reaction constants B and B/A are 2×10^{-4} m^2h^{-1} and 8×10^{-3} mh^{-1}, respectively and they are comparable with those in the oxidation reaction of silicon wafer at same temperature. The reaction between gas phase and silicon may be the rate determining step in the beginning of the reaction. In longer time, the diffusion of nitrogen may be the rate determining step.

Characterization of films: Infrared spectra of films obtained by nitriding silicon wafer with nitrogen or nitrogen-hydrogen plasma for 4hours are listed in Table 2. For the sample obtained by the reaction with nitrogen plasma, strong absorption peaks at 1160 cm^{-1} of Si-O stretching and at 450 cm^{-1} of O-Si-O bending were observed. So the silicon wafer was oxidized by the reaction with nitrogen plasma. For the sample obtained by the reaction with nitrogen-hydrogen plasma, strong absorption peaks at 850 cm^{-1} of N-Si-N bending were observed. The peaks based on Si-O bond disappeared and Si-N bond was only formed. The spectra was similar to that of Si_3N_4 film obtained by CVD. According to electron diffraction the films obtained by nitriding silicon wafer with nitrogen-hydrogen plasma showed halo pattern. These films were amorphus.

Diagnostics of plasmas: The emission spectra from nitrogen and nitrogen-hydrogen plasmas during the reaction with silicon wafer were observed with monochrometer. Electronic transition observed from 700 to 200 nm are listed in Table 3. In the spectra from nitrogen plasma, the first positive system, the second positive system and the fourth positive system of N_2 and the first negative system and Janni-D'Incan system of N_2^+ were observed. Moreover, in the lower wave length region, γ-system of NO and some line spectra of silicon were observed. In thr spectra from nitrogen-hydrogen plasma, the second positive system and the fourth positive system of N_2 were observed. The first negative system and Janni-D'Incann system of N_2^+ were considerably decreased and $\Delta v=0$ (0-0,1-1) sequences of the first negative system was only detected. $A^3\Pi-X^3\Sigma^-$ electronic transition of NH and some line spectra of hydrogen and nitrogen were detected. The spectra of NO and silicon could not be detected. The vibrational temperature, Tv, of N_2 and N_2^+ in the nitrogen plasma and that of N_2 in in the nitrogen-hydrogen plasma were determined from the relative values of of the band intensity of the sequences $\Delta v=+1$ and -2 of the system $C^3\Pi_u-B^3\Pi_g$ of N_2 and $\Delta v=-1$ of the system $B^2\Sigma_u^+-X^2\Sigma_g^+$ of N_2^+ (8,9). Results obtained are listed in Table 4. Tv of N_2^+ was higher than that of N_2 in the nitrogen plasma and Tv of N_2 in the nitrogen plasma was higher than that in the nitrogen-hydrogen plasma.

The ionic species in the plasmas were extracted through 30 m orifice by differential pumping. A pressure in the analyzing chamber was maintained below 10^{-4} Torr. For nitrogen plasma, N^+, N_2^+ and NO were identified with H^+, H_2^+ and O_2^+ which were produced from residual gases. For nitrogen-hydrogen plasma, H^+, H_2^+ and nitrogen-hydrogen molecular ions, NH^+, NH_2^+, NH_3^+, were identified in addition to N^+ and N_2^+.

Electron energy, kTe, and ion density, ni, of the plasma over the silicon wafer during nitriding were measured by means of electric double probe technique. kTe was between 4 and 9 eV for nitrogen plasma and between 4 and 14 eV for nitrogen-hydrogen plasma. n_i was 10^8 - 10^{10} cm^{-3} for both plasmas and a degree of ionization was order of 10^{-8} -10^{-6}.

Discussion of Reaction; In this study, the presence of silicon and NO was detected in the nitrogen plasma. Silicon and NO was completely suppressed in the nitrogen-hydrogen plasma. In the nitrogen plasma, N_2^+ was accelerated by the potential difference between plasma and wall (10) and impinged the wall of the chamber. So sputtering of SiO_2 from the wall would occur. SiO_2 would react wuth N_2 in the plasma, then NO and silicon would be formed. By the reaction between the nitrogen plasma and the silicon wafer, silicon surfacewas oxidized with NO. By the reaction between the nitrogen-hydrogen plasma, silicon wafer was nitrided with N_2 and NH in the plasma because of suppression of NO.

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Table 1 Film thickness and refrective index of silicon wafer after nitriding with nitrogen-hydrogen plasma

Nitriding time (h)	Film thickness (A)	Refrective index
0.5	82	1.77
1.0	97	2.10
1.5	163	2.00
2.0	180	1.97
3.0	202	2.00
4.0	245	1.99
8.0	356	2.03

Table 2 Infrared absorption peaks of silicon wafer after reaction with nitrogen and nitrogen-hydrogen plasmas

Samples	Wave number (cm^{-1})	Identified mode
CVD Si_3N_4	840	Si-N stretching
	480	N-Si-N bending
Reaction with nitrogen plasma	1160	Si-O stretching
	840	Si-N stretching
	450	O-Si-O bending
Reaction with nitrogen-hydrogen plasma	880	
	850	Si-N stretching
	840	
	480	N-Si-N bending

Table 3 Electronic transitions observed in the emission spectra of plasmas

Plasma gas	Observed transition from 7000 to 2000 A	
Nitrogen	N_2, $B^3\Pi_g - A^3\Sigma_g^+$	Δv = 3,4 (v'=13)
	N_2, $C^3\Pi_u - B^3\Pi_g$	Δv =-7 - +3 (v'=11)
	N_2, $D^3\Sigma_u^+ - B^3\Pi_g$	Δv =-4 - -1 (v'=4)
	N_2^+, $B^2\Sigma_u^+ - X^2\Sigma_g^+$	Δv =-2 - +2 (v'=4)
	N_2^+, $D^2\Pi_g - A^2\Pi_u$	Δv =-2 - +2 (v'=7)
	NO, $A^2\Sigma^+ - X^2\Pi$	Δv =-5 - +2 (v'=6)
	Si	
Nitrogen-Hydrogen (4:1)	N_2, $C^3\Pi_u - B^3\Pi_g$	Δv =-7 - +3 (v'=11)
	N_2, $D^3\Sigma_u^+ - B^3\Pi_g$	Δv =-4 - -1 (v'=4)
	N_2^+, $B^2\Sigma_u^+ - X^2\Sigma_g^+$	Δv =0 (0-0, 1-1)
	NH, $A^3\Pi - X^3\Sigma^-$	Δv =0 (0-0, 1-1)
	N, 2P-2S^o	
	H, H_α, H_β, H_γ	

Table 4 Vibrational temperature of molecular species in plasmas

Plasma gas	Transition		Temperature (K)
Nitrogen	N_2, $C^3\Pi_u - B^3\Pi_g$,	Δv =-2	5400
		Δv =+1	4400
	N_2^+, $B^2\Sigma_u^+ - X^2\Sigma_g^+$,	Δv =-1	5700
Nitrogen-Hydrogen (4:1)	N_2, $C^3\Pi_u - B^3\Pi_g$,	Δv =-2	4000
		Δv =+1	3800

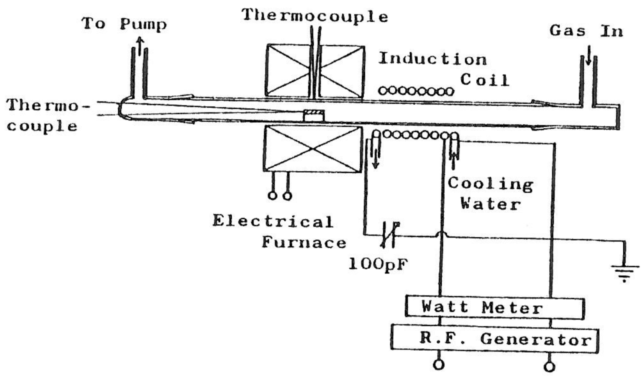

Fig. 1 Reaction apparatus

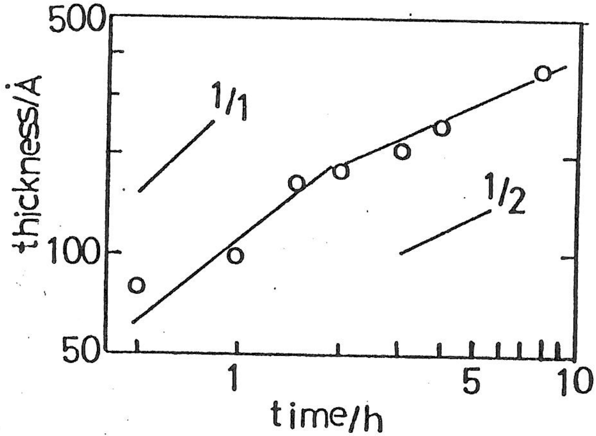

Fig. 2 Film thickness vs. reaction time