NITRIDING OF SILICON IN RF INDUCED NITROGEN PLASMA

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ABSTRACT

The nitriding of silicon wafer of semiconductor grade was tried in rf glow discharge of nitrogen at low pressures. By AES of the wafer treated for 4 hrs at input power of 740W, nitrogen was detected with a constant atomic ratio of N/Si in the surface layer. The nitriding was accelerated by adding a suitable amount of helium or hydrogen into nitrogen. The electron temperature and the electron or ion density were determined by a double probe.

1. INTRODUCTION

It is very difficult to nitrify directly the surface layer of high purity silicon by heating in nitrogen atmosphere. A very thin and inhomogeneous layer of silicon nitride was obtained at 1150-1375°C in nitrogen atmosphere (1). The nitride layer obtained by using deoxidized and dried nitrogen was homogeneous and amorphous when the thickness was less than 10nm(2). The structure of the layer changed into polycrystal from amorphism when the thickness was over 10nm. The nitride layer of 25nm thickness was formed by 20 hrs nitriding at 800°C in NH_3 atmosphere(3). Only very thin oxi-nitride layer of 5-6nm thickness was formed at 1100°C for 3-16 hrs by using NH_3 or NH_3-Ar (4).

The purpose of our study is to investigate whether the nitriding of silicon wafer in an electrically isolated state is possible in r.f. induced nitrogen discharge. In our previous experiment, the nitriding of electtrolytic iron plate was carried out successfully below 550°C in r.f. nitrogen discharge. Therefore an unique effect of r.f. nitrogen plasma for the nitriding of silicon wafer at low temperatures can be expected and the characteristics of the plasma must be analysed in connection with the nitriding.

2. EXPERIMENTAL

2-1. Apparatus and Procedure in Preliminary Experiments

Fig.1 is a schematic diagram of apparatus for preliminary experiment. The length and the inner diameter of the transparent quartz reactor tube were 1000 and 16.5mm respectively, but another quartz tube of length 1000mm and inner diameter 26.5mm was also used. Stainless steel caps were attached to the both ends of the reactor tube with heat-resisting O rings for seal. The port B was used for diagnostics of plasma by a double probe. The maximum output power of r.f. generator was 500W. Five or Seven turned r.f. coil of copper tube of inner diameter 6mm covered with glassy ribbon was set at the middle part of the reactor tube. The dimension of r.f coil was 40mmϕx37mm or 30mm x54mm. High pure gases (Ar;99.998%, N_2;99.998%, H_2;99.999%, He; 99.995%) and ultra high pure gases (N_2;99.9998%, H_2;99.9999%) were supplied to the reactor tube through a bubbling flask, a float flowmeter and a trap (not shown in Fig.1) cooled with liquid nitrogen set at the gas inlet of the reactor tube from gas cylinders. A rotary vacuum pump with a nominal evacuation speed of 50l/min was operated to reduce the inner pressure of the reactor tube. The second trap with liquid nitrogen was set between the reac-

tor tube and the vacuum pump to prevent a back flow of oil vapor. The flow rate of gas was controlled by a teflon needle valbe. The pressure was measured by a Macleod vacuum gauge. The third trap with liquid nitrogen was set between the reactor tube and the vacuum gauge to prevent a back flow of Hg vapor.

P and n type silicon wafers of each diameter 3" and 2" were offered by Nippon Silicon Co.. The one side of each wafer was in a state of mirror surface by polishing. The chemical composition and physical properties of the wafers are shown in Table 1. Each wafer was divided into small samples along its cleavage plane. Thus two kinds of small samples of the dimensions 15x10mm and 20x10mm were prepared. This sample was placed on an alumina boat or a quartz plate and set in the reactor tube as shown in Fig. 2. The reaction tube was evacuated and displaced with hydrogen, prior to the nitriding treatment. Such operation was repeated three times. Then the sample was exposed to hydrogen discharge for 0.5-1 hrs at the same pressure as that in the following nitriding treatment. The surface of silicon was purified by such pre-treatment. X-ray diffraction analysis, optical microscopy, SEM and AES of the sample were carried out after its nitriding.

2-2. Apparatus and Procedure in Main Experiments

Fig. 3 shows a schematic diagram of the apparatus for the main experiment. The length and the inner diameter of a quartz reactor tube were 1000mm and 35.0mm respectively. The nominal maximum output power of the r.f. generator was 2KW. A five-turned r.f. coil consisted of 6mm copper tube was set at the middle outer part of the reactor tube. The type of this coil was somewhat different from that of the coil used for preliminary experiment as shown in Fig. 3. The both ends of the reactor tube were cooled by a water jacket composed of a heat-resisting tube (CALOREX RED) with semicircular section. Ultra pure nitrogen (99.9995%), hydrogen (99.9999%) and helium (99.995%) were dried and deoxdized by passing them through a dry-column GCD of Taiyo Oxygan Co. make and a deoxidizing column OXISORB-L of Messer Griesheim LTD make. A filter (NUPRO B-4FR-15) was used for removal of ultra fine dust in passing gas. The pressure was measured by Pirani gauge GP-2T of ULVAC make.

P-type silicon wafers of diameter 4" with a polished mirror surface offered by Nippon Silicon Co., were divided into small samples of the dimension of 10x20-25mm along the cleavage surface. The chemical composition and physical properties of these silicon wafers were shown in Table 2. Some samples were immersed for 1 minute in 56% HF solution and cleaned with running water before the nitriding treatment, but most samples were used without such purification pre-treatment.

2-3. Double Probe

The electron temperature and the electron density or ion density in nitrogen plasma were determined by a simple double probe. Two electrodes of the double probe are consisted of two tungsten wires of diameter 0.5mm sealed in a pyrex glass tube of diameter 9mm. The effective length and the distance between two electrodes were 8-15mm and 1-6mm respectively. The probe was removable along the center line of the reactor tube, but it was modified to be able to move radially inside the reaction tube as shown in Fig. 4. The double probe was connected to a simple circuit for measurement of d.c. voltage and current, which was equipped with a filter to remove r.f. noise.

3. RESULTS AND DISCUSSIONS

3-1. Preliminary Experiment

The nitriding was carried out for 1, 4, 8, or 10 hrs at a constant

pressure between 21 and 400pa and a gas temperature between 440 and 480°C in nitrogen-hydrogen discharge (N_2 H_2=1 1) with an input power between 115 and 365W. In some cases, a copper net was set and heated at the distance 30mm toward the gas inlet (the right side of the reactor tube shown in Fig. 1) from the sample to decrease oxygen potential of supplied gases.

The maximum thickness of a thin film formed on the sample by this treatment was estimated to be about 1 μm from some interference color change observed in the surface of the sample placed near the r.f. coil. But the film was not formed in the presence of a brilliant ring discharge (we call it arc discharge) generated in the central part of r.f. coil at a higher power input. A very weak X ray diffraction line from α-Si_3N_4 (200) was detected in a few samples. Two typical scanning electron micrographs are shown in Fig.5 and Fig.6. Many spherical projections were observed on the surface. Fig.6 shows that some projections pealed off from the surface. The thickness of the projection can be estimated to be about 200nm from this figure. Such projections seem to be a gas bubbles.

3-2. Main Experiment

Three small silicon samples set on a sample holder as shown in Fig.7, were placed in the reactor tube. The middle sample was just positioned at Z=0, that is the right end of the r.f. coil (the gas inlet side of the reactor) as shown in Fig. 3. Accordingly the left sample and the right sample were positioned at Z=-20mm and +20mm respectively, that is, the distance from the right end of the coil. Thus the left sample is situated inside the coil.

The nitriding conditions are as follows:gas flow rate-- N_2(25 1/min)+H_2(0,25, 75 1/min), N_2(50 1/min)+H_2(0, 50, 150 1/min), N_2(75 1/min)+H_2(25 1/min), N_2(100 1/min)+H_2(0, 100 1/min), N_2(150 1/min)+H_2(0,50 1/min), N_2 (200 1/min)+H_2(0 1/min), pressure--63-330 Pa, input power--370-740W, time --4 hrs.

The surface color of the sample changed depending on its position in the reactor tube. The interference color appeared on the surface in nitrogen-hydrogen discharge. The mirror surface was maintained as it was in the nitriding by pure nitrogen plasma. Typical optical microphotographs showed many small ring patterns on the surface treated in nitrogen-hydrogen plasma, while such patterns were not observed on the mirror surface. The surface structure with such ring patterns was resemble to that shown in Fig.5 and Fig.6. This fact suggests that hydrogen plays an important role for such structure formation. The results of AES of the sample without the nitriding treatment showed the presence of oxygen. Here Ar ion etching was practiced. Therefore a origin of such oxygen may be the AES apparatus itself, because the lowest pressure in its sample room is at most $1x10^{-6}$ Pa and the heating system of the sample is not equipped. Two examples of AES of the treated samples are shown in Fig.8. Both samples were treated at Z=0 and 740W. There appeared a general tenden y showing that the thickness of the nitride film increased with the increase of hydrogen content in the discharge, which meaned the increase of the nitriding rate. But a wide range without a constant atomic ratio of S/N was detected at the boundory between the nitride film and silicon wafer as illustrated in Fig.8. Fig.9 shows that the thickness of the nitride film is not uniform depending on the surface position. The figures in each small squares shows the Ar etching time elapsed until nitrogen can not be detected any longer. The relation between the ion etching by Ar ion and the thickness of the nitride film can be obtained from the estimated index of the film by comparing the interference phenomena of the nitride film and a thin oxide film on Si wafer(6). The maximum thickness of silicon nitride film formed in pure nitrogen discharge was estimated to be about 280nm after 4 hrs treatment at 740W. In the latest ex-

periment at 67Pa and 740W in nitrogen-helium(N_2:H_2=1:4) discharge, the thickness of amorphous nitride film reached 400-500nm. A favorite effect of He addition to nitrogen for nitride film formation was made clear from such result.

3-3. Diagnostics of r.f. nitrogen discharge by double probe

Fig.10 shows the change of the plasma density measured when the probe was shifted horizontally along the center line of the reactor tube. The electron temperature along this center line did not hardly depend on the position and the input power. Examples of the distributions of the electron densities, the plasma densities and the relative floating potentials are shown in Fig. 11 and 12. Such tendency of the change of the electron temperature and plasma density in the radial direction of the reactor tube can be expected from the theory of positive column in glow discharge.

The electron density and the plasma density in nitrogen-helium discharge were much larger than those in pure nitrogen discharge. The electrons with high energy seems to be effective to activate and dissociate nitrogen molecule. The activation and ionization of nitrogen molecule may be accerated by Penning effect of activated helium atom. The reason why the nitriding proceeded effectively in nitrogen-hydrogen discharge may be explained by such considerations. It is probable that the inhomogeneity of plasma characteristics made clear by these double probe measurements causes the uneven thickness of the nitride film on the surface of the same sample, but it was proved that such film has a good CV characteritic for MIS.

4. CONCLUSION

The amorphous silicon nitride film was formed by nitriding of silicon waferin nitrogen and nitrogen-helium glow discharge. A good effect of helium addition to nitrogen could be related with the double probe measurements of plasma characteristics.

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Table 1. Chemical composition and physical properties of p-type and n-type Si wafers used in preliminary experiments

B 5×10^{14}, C<$1\times10^{16-17}$, O<1.5×10^{18}, Heavy Metals<$1\times10^{11-12}$atoms/cc
Resistivity:7-9Ω·cm, EPD:0, Surface:(110), Thickness:370μm (P-type)
Sb 1×10^{19}, C $1\times10^{16-17}$, O 1.5×10^{18}, Heavy Metals<$1\times10^{11-12}$ atoms/cc
EPD:0, Surface:(111), Thickness:290μm, Resistivity:5-15$\times10^{-3}$Ω.cm (n-type)

Table 2. Chemical composition and physical properties of p-type Si wafers in main experiments

B 1.25×10^{15}, C<3×10^{16}, O<$1-2\times10^{18}$, Heavy Metals unknown, Resistivity :10±1Ω·cm, EPD: 0, Surface:(100), Thickness:625±10μm

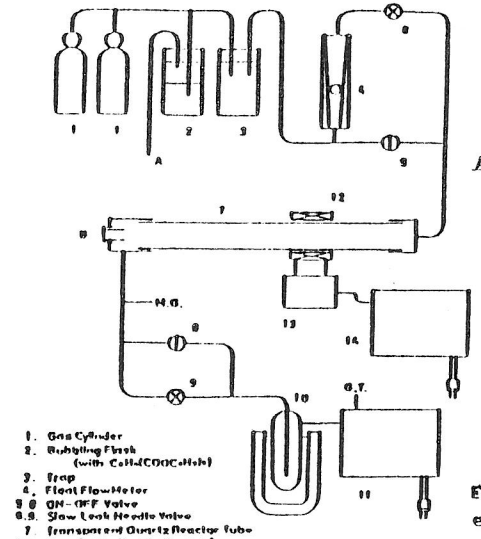


Fig.1. Schematic diagram of apparatus for preliminary nitriding experiments.

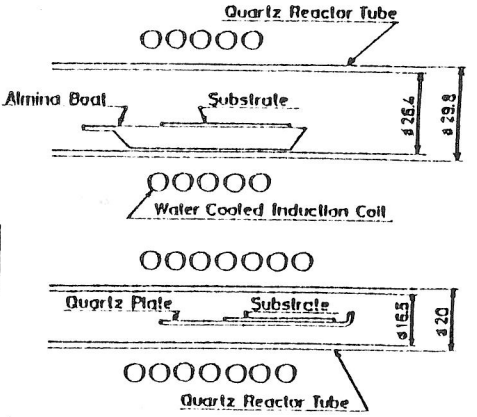
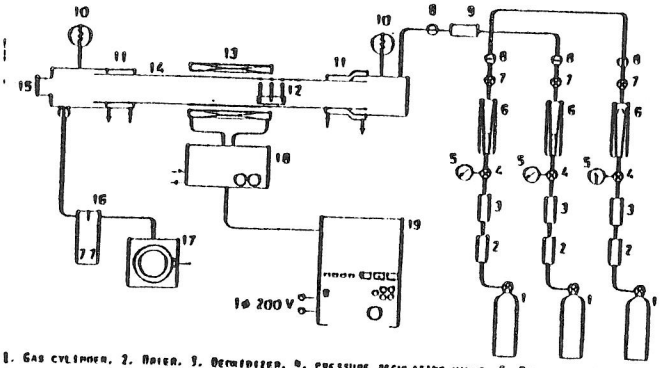


Fig.2. Sample holders in preliminary experiments.



1. Gas cylinder. 2. Dryer. 3. Dehydrator. 4. Pressure regulating valve. 5. Pressure gauge. 6. Float flow meter. 7. Metering valve. 8. Stop valve. 9. Gas mixing filter. 0. Pirani gauge. 11. Water-cooling jacket. 12. Samples & holder. 13. Water-cooled R-F induction coil. 14. Quartz tube. 15. Viewing port. 16. Trap. 17. Rotary pump. 18. Matching box. 19. R-F generator.

Fig.3. Schematic diagram of apparatus for main nitriding experiments.

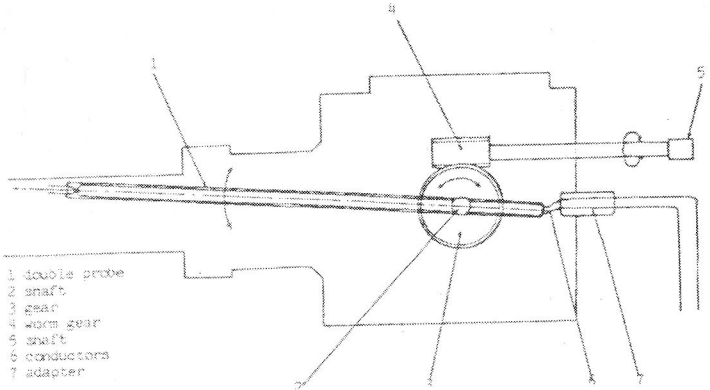


Fig.4. Double probe modified for radial measurement.

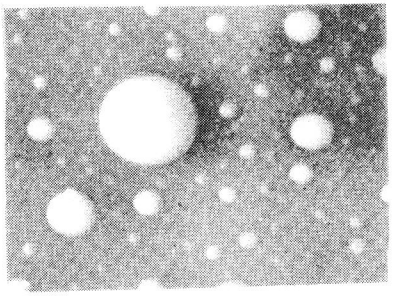


Fig. 5. SEM of Si surface after nitriding.

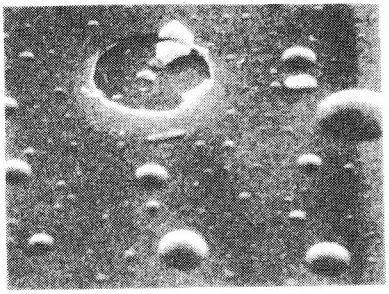


Fig.6. SEM of Si surface after nitriding (45°tilt).

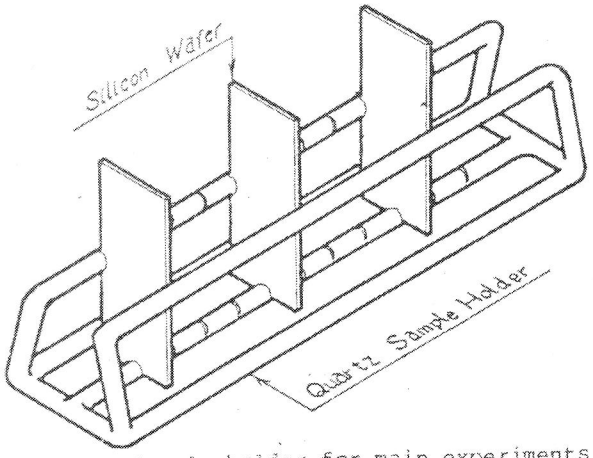


Fig. 7. Sample holder for main experiments.

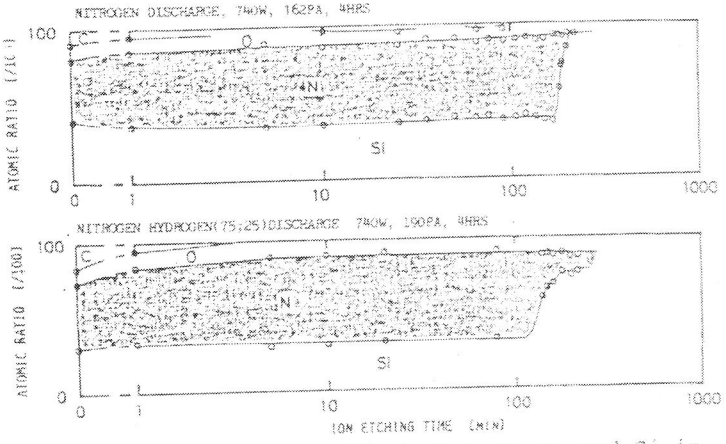


Fig.8. Concentration profiles of C, O, N, and Si in nitride films of Si , wafers.

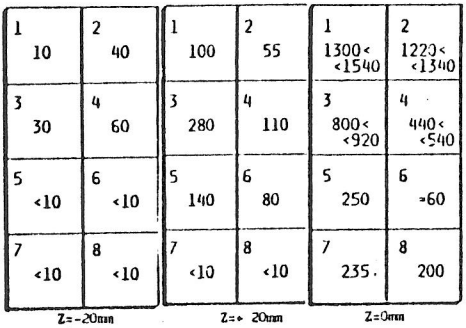


Fig.9.Distribution of thickness of nitride film on Si wafers (rf nitrogen plasma treatment at 63Pa and 740W for 2 hours) as argon etching time in minutes.

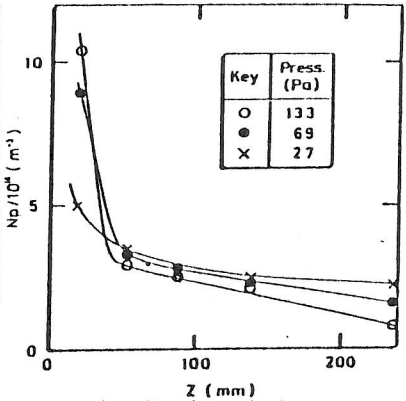


Fig.10. Distribution of plasma (electron)density of rf nitrogen plsma at power input 130W along the center line of plasma reactor.

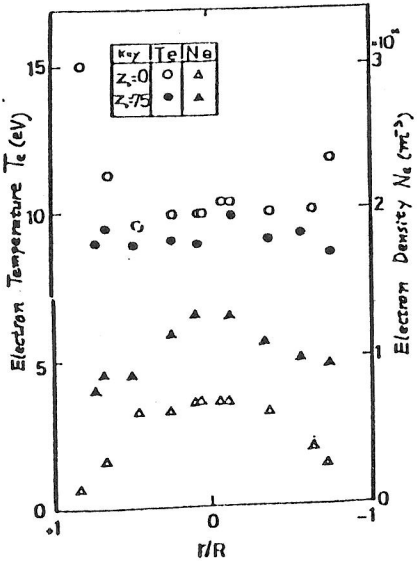


Fig.11. Radial distribution of electron temperature and plasma (electron) density of rf nitrogen plasma at power inrut 120W and pressure 82Pa.

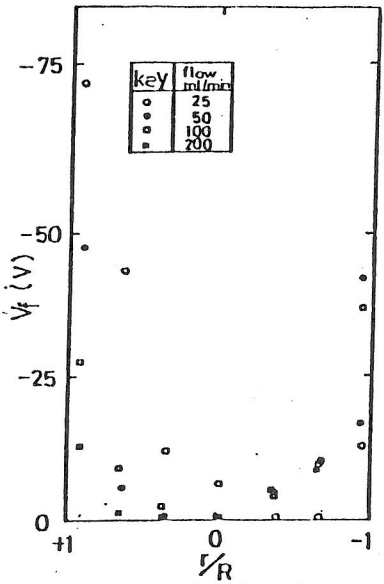


Fig.12. Radial distribution of relative floating potential V_f of rf nitrogen plasma at power input 120W and pressure 82Pa.