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Low Temperature Nitridation of Silicon by Excimer Laser Irradiation

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Silicon direct nitride films were grown in purified ammonia gas at a substrate temperature of 400°C and an excimer laser pulse energy of 15 mJ/cm^2 with the substrate held normal to the incidence laser pulse, in contrast with the substrate held parallel to the incident laser pulse. The temperature rise induced by the laser was calculated and found that the thermal effect of the laser irradiation was of little significance in this experiment. The optimum ammonia pressure was found for nitridation. These results suggest that irradiation by the laser to weaken bonds between silicon atoms as well as the photodissociation of ammonia molecules was prerequisite for silicon nitridation.

1. Introduction

In the past few years, extensive research has been done on the use of light irradiation to process semiconductor materials. Infrared, visible, and ultraviolet light sources are successfully used to induce excitation and photodissociation of molecules. The interest underlying this research is largely motivated by the desire to reduce wafer processing temperature and eliminate discharge processes. Deposition of amorphous silicon, silicon dioxide, silicon nitride, and some metals has been extensively investigated so far. In the research, substrates on which films are deposited are little concerned with the light irradiation. On the other hand, some researchers utilize light irradiation to generate electron-hole pairs, not photodissociate molecules. Young et al. reported that silicon oxidation was enhanced by an Ar ion laser irradiation which has no photochemical effect.[1] They speculated that weaken bonds between silicon atoms by light irradiation were the cause of the enhancement.

In this paper low temperature silicon nitridation using an ArF excimer laser and highly purified ammonia gas is described. This new silicon nitridation technique utilizes both effects mentioned above. That is, an ArF excimer laser with a wavelength of 193 nm was used to photodissociate ammonia molecules and generate electron-hole pairs near a substrate surface to weaken bonds between silicon atoms.

2. Photochemistry of ammonia

Figure 1 shows the absorption coefficient of ammonia gas in the region of 170 nm to 210 nm.[2] Ammonia gas has a high absorption coefficient of around 100 atm^{-1}cm^{-1} at wavelength of 193 nm obtained from an ArF excimer laser. This absorption corresponds to transition from a ground state of ammonia to an upper electronic state.[3]

$$NH_3(\tilde{X}^1A_1') \longrightarrow NH_3(\tilde{A}^1A_2'') \quad (1)$$

The dissociation from this state is represented by the following reactions.

$$NH_3(\tilde{A}^1A_2'') \longrightarrow NH_2(\tilde{X}^2B_1) + H \quad (2)$$

$$NH_3(\tilde{A}^1A_2'') \longrightarrow NH(a^1\Delta) + H_2 \quad (3)$$

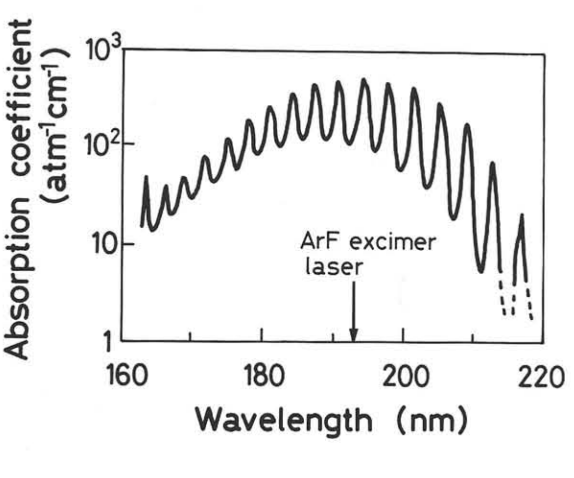

Fig.1 Absorption coefficient of ammonia gas.

Therefore, reactive radicals, NH_2 and NH, which will easily react with a silicon surface are efficiently generated by an ArF excimer laser.

3. Experimental setup

A schematic illustration of the experimental setup is shown in Figure 2. The laser beam, reflected by a multicoated dielectric mirror, was led into the reaction chamber through a window made of fused quartz, irradiating a silicon substrate almost normally. The reaction chamber is equipped with a mechanical pump and a cryo-pump which can evacuate up to 2×10^{-5} Pa. To monitor photochemical products, a quadrupole mass analyzer was used. The setup allows substrates to be heated from the back by infrared lamps and moved 1 cm/sec by an X-Y stage. The excimer laser was operated at a 12 ns pulse width with a 12 or 25 Hz pulse repetition rate.

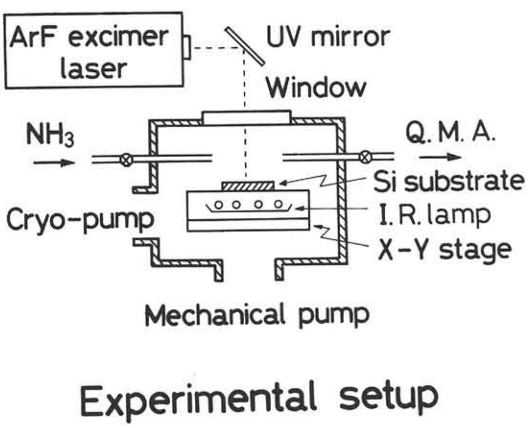

Fig.2 Schematic illustration of experimental setup.

4. Simulation of temperature rise induced by the laser

First, temperature rise at the substrate surface irradiated by the laser was calculated. In this experiment the laser beam dimension is in the order of square cm, so it is a good approximation to treat the heat diffusion equation in one dimension. Because the thermal-diffusion coefficient is strongly dependent on temperature, it can be approximated by

$$D(T) = \frac{Dr}{1 + aT} \qquad (4)$$

$$Dr = 0.94\ cm^2 sec^{-1}, \quad a = 0.0072\ /C$$

where T is the substrate temperature with no laser irradiation.[4,5] Figure 3 shows a simulation result of temperature rise at the end of one ArF excimer laser pulse under conditions used in our experiment. The maximum temperature rise is at most 55°C. Therefore, the thermal effect induced by the laser irradiation is of little significance in this experiment.

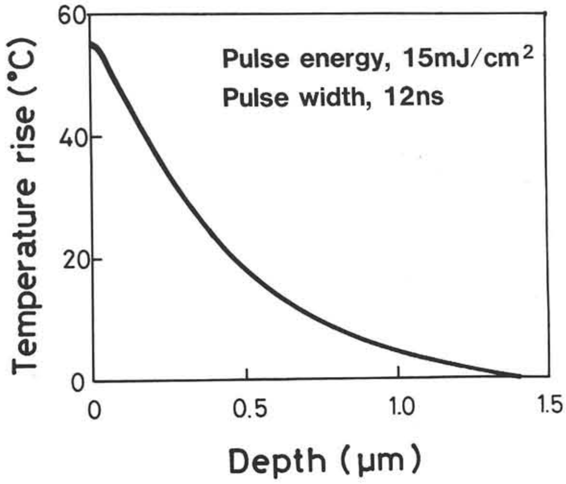

Fig.3 Temperature rise profile at the end of one ArF excimer laser pulse with a energy of 15 mJ/cm^2 and a pulse width of 12 ns.

5. Analysis of grown films

The grown films were analyzed by Auger electron spectroscopy and X-ray photoelectron spectroscopy. Figure 4 shows the Auger electron spectroscopy spectrum of a sample surface irradiated at normal incidence by about 1500 pulses of 15 mJ/cm^2. The substrate was kept at 400°C. For comparison, a spectrum of a sample kept at 400°C in the ammonia gas for 10 minutes with no laser irradiation is also shown. It is obvious that no signal of elemental silicon which appears at 92 eV is seen in the spectrum of an excimer laser enhanced nitrided film. This means that the sample surface is fully covered with silicon nitride or silicon oxynitride. In case of a sample with no laser irradiation, less nitrogen is detected and the signal of elemental silicon is large. From this figure, we can see the drastic enhancement of nitridation by an ArF excimer laser. It was also found that a substrate held parallel to the incident laser beam produced no enhancement of nitridation. Therefore, the effect of the laser irradiation of a silicon substrate is prerequisite for nitridation using the laser. Figure 5 shows an X-ray photoelectron spectroscopy spectrum of a sample surface irradiated by the laser at normal incidence. The binding energy of N_{1s} is 397 eV, which is the same energy as one obtained from plasma-enhanced thermally nitrided silicon films.

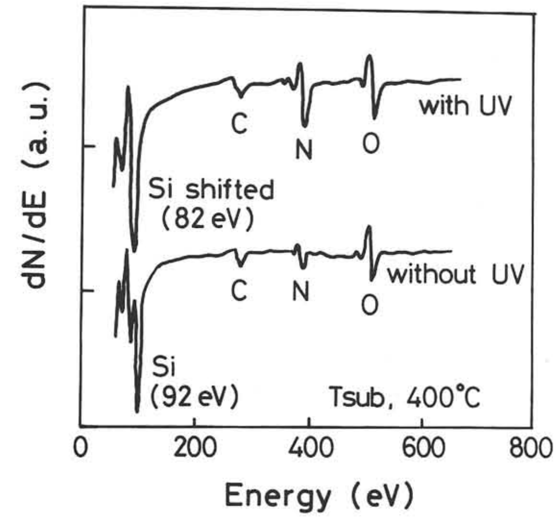

Fig.4 Auger electron spectroscopy spectra obtained with and without ArF excimer laser irradiation.

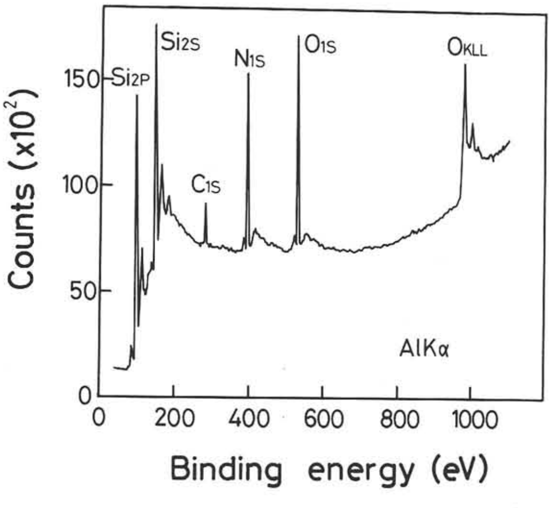

Fig.5 X-ray photoelectron spectroscopy spectrum obtained with ArF excimer laser irradiation.

6. Nitrogen fraction of grown films

Nitrogen fraction of grown films in various ammonia pressure were measured by Auger electron spectroscopy. From Figure 6, the maximum nitrogen fraction is obtained at a pressure of 1.3 Pa. This was interpreted as follows. At pressure lower than 1.3 Pa, NH and NH_2 radical concentrations are low because of low concentration of ammonia molecules. At the higher pressures more laser energy is absorbed in the gas before it reaches the substrate surface, which causes lack of weaken bonds between silicon atoms. Therefore, nitridation was not enhanced in these two ammonia pressure regions.

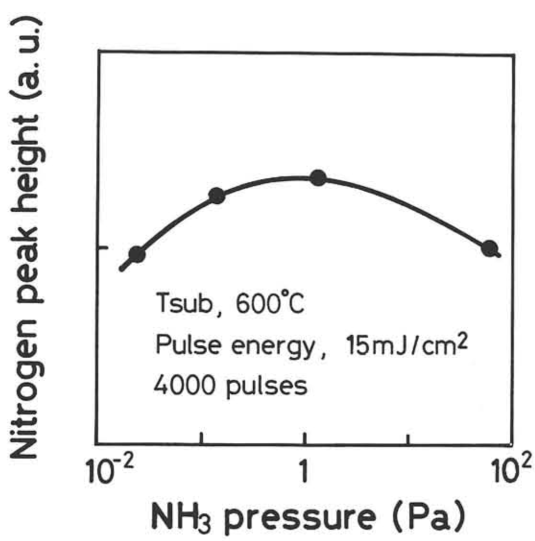

Fig.6 Nitrogen fraction of films grown in various ammonia pressures, measured by Auger electron spectroscopy.

7. Breakdown strength of laser enhanced nitrided films

The breakdown strength of laser enhanced nitrided films were studied with MNS diodes. The substrate used was p-type Si(100) wafer of 1 Ωcm. The wafer was irradiated under ammonia pressure of 1 Pa by 6000 pulses of 15 mJ/cm^2 at a substrate temperature of 600°C. The Al electrode , 400 μm in diameter, was patterned by wet etching. The breakdown strength histogram is shown in Figure 7. Although there is a broad profile in the breakdown strength, most diodes have breakdown strength of around 15 MV/cm. This result indicates rather high dielectric strength than that of a thermally nitrided film.

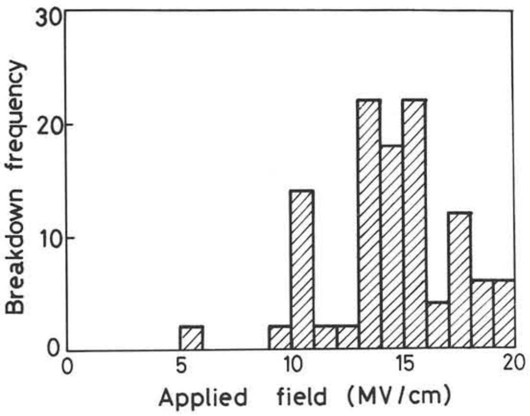

Fig.7 Dielectric breakdown strength histogram of MNS diodes.

8. Conclusion

Direct silicon nitridation was enhanced under ArF excimer laser irradiation. Direct silicon nitrided films were obtained at a substrate temperature of 400°C with laser irradiation at normal incidence. The optimum ammonia pressure was found for silicon nitridation. Irradiating by the laser to weaken bonds between silicon atoms as well as the photodissociation of ammonia molecules was prerequisite for silicon nitridation. Dielectric properties are superior to those of previously reported thermal nitride films.

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