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A new procedure for plasma-enhanced thermal nitridation of silicon is reported. Highly purified ammonia plasma is generated in a quartz tube by radio-frequency power heating induction-coupled and SiC-coated carbon susceptors. This system requires no additional electrode in the reaction environment. At a substrate temperature of 1050 °C, thermal silicon nitride films with a thickness above 100 Å are grown for 150 min in background pressures ranging from 10^{-1} to 10 Torr. The films have a refractive index of 1.90, oxygen contamination of less than 10%, and an etching rate two orders of magnitude smaller than that of a thermal SiO_2 film in a solution of NH_4F:HF = 7:1.

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Thermally grown silicon nitride films with high uniformity and dense structure have been of increasing interest for LSI processing.[1,2] Thermal nitridation of silicon in purified nitrogen or ammonia gas was originally reported to require relatively high temperatures around 1200 °C.[1-5] The attainable thickness of thermal nitride films was limited to much less than 100 Å when a nitridation process similar to the conventional thermal oxidation of silicon was used. More recently, Chang *et al.*[6] studied plasma nitridation of silicon at substrate temperatures below 600 °C with fluorine used to enhance film growth. Although some of the fluorine was incorporated and N/O concentration ratio was near 2, uniform films with thicknesses above 1000 Å were grown in about 4 h.

This letter describes a new procedure for plasma-enhanced thermal nitridation of silicon. Ammonia plasma is generated on or near silicon surfaces which are radio-frequency (rf) heated at specific temperatures above 600 °C. Film properties are close to stoichiometric Si_3N_4. In this manner, thermal nitride films thicker than 100 Å can be obtained under the conditions acceptable to conventional LSI fabrication processes.

Chemically cleaned silicon wafers mounted on silicon carbide-coated carbon susceptors were loaded into a horizontal quartz tube. Its diameter and length were 125 and 905 mm, respectively. Highly purified ammonia gas was introduced into the tube at reduced pressures ranging from 10^{-1} to 10 Torr. A rf power of 5–15 kW at a frequency of 400 kHz was applied to heat the induction-coupled susceptors while glow discharge was generated around the susceptors. The ammonia gas was activated by the rf power. Electron density in the ammonia plasma is expected to range from 10^9 to 10^{12} cm^{-3}. This nitridation system is far different from that used by Chang *et al.*,[6] where the substrate was biased to collect the plasma. The present system uses no additional electrode in the reactor tube, which produces a cleaner environment. Another advantage of this method is that batch production for many wafers becomes possible. It should be noted that the purity of the ammonia gas is important to reduce oxygen contamination in the thermal nitride films. In this experiment, ammonia gas with 99.999% purity was further purified with synthesized zeolites. However, impurity levels of oxidants in the ammonia gas were indeterminable because water, the most dominant impurity, was probably in the form of ammonium hydroxide. Carrier gases such as nitrogen, argon, and hydrogen were also used but there was no distinct improvement in properties of films grown in those gases.

Thermally nitrided silicon surfaces in the ammonia plasma exhibited amorphous structure and no morphology under a wide range of growth conditions. Figure 1 shows the time dependence of film thickness at a substrate temperature of 1050 °C. The films were grown at a background pressure of 1 Torr. Figure 1 also shows thermal nitridation with non plasma at 1200 °C as a reference. Film thicknesses were measured by ellipsometry with a wavelength of 5461 Å. In the case of nonplasma, the maximum thickness is limited to about 50 Å after a reaction time of 200 min. The activation energy for the thermal reaction between silicon and ammonia in nonplasma state was calculated from the Arrhenius plot to be 0.2 eV. This small value makes it impossible to obtain films much thicker than 50 Å even if the substrate temperature is increased above 1200 °C. Figure 1 demonstrates that rf-activated ammonia plasma can be used effectively to enhance the maximum thickness to greater than 100 Å. At the initial stages of both plasma and nonplasma cases,

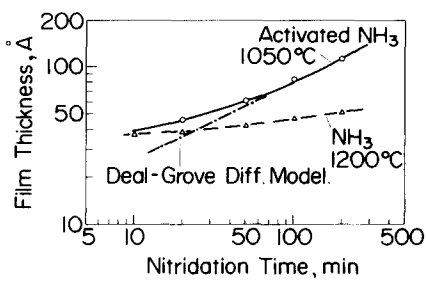

FIG. 1. Thermal nitridation of silicon in rf-activated ammonia gas at 1050 °C and in nonactivated ammonia gas at 1200 °C.

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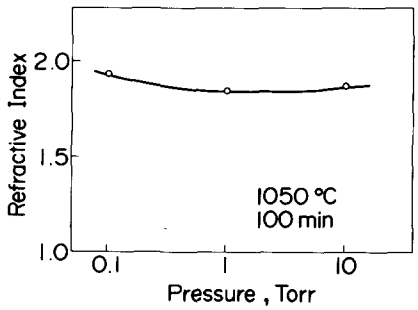

FIG. 2. Refractive indices vs background pressure of thermal nitridation at 1050 °C for 100 min.

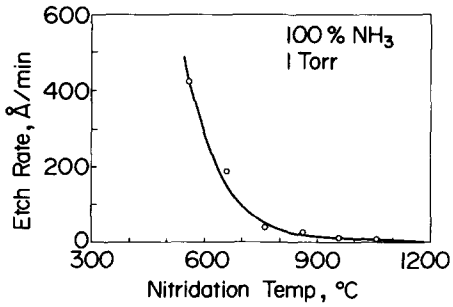

FIG. 4. Etching rates of thermal nitride films in a solution of NH_4F:HF = 7:1 vs nitridation temperature.

the film growth seems to follow a reaction-limited process up to a thickness of about 30 Å, as growth is rapid and uncontrollable. During the later stages to growth, the nitridation in the ammonia plasma appears to follow a diffusion-limited process where active nitrogen atoms from the ammonia plasma play an important role. The growth relation may partially match the Deal-Grove diffusion model.[7] The growth rate of thermal nitride films is quite independent of the pressure in the range of 10^{-1} to 10 Torr and the ammonia flow rate from 10 to 1000 cm^3/min. The growth rates of thermal nitride films for both plasma and nonplasma cases are much smaller than those of thermal oxide films. This feature allows better control of the thickness of thermal nitride films. Reproducibility in film thickness is much better than $\pm$ 5 Å among lots.

Refractive indices were measured by ellipsometry with a wavelength of 5461 Å. Obtained values with respect to the background pressure are shown in Fig. 2. Nitridations for those films were performed at 1050 °C for 100 min. It is apparent that the indices around 1.90 are unaffected by the pressure. The values are very near to the value of the stoichiomnetric Si_3N_4. Although chemically vapor deposited (CVD) nitride films were reported to have indices close to 2.00, this was not the case for films thinner than 100 Å. Recently, Andrews *et al.*[8] reported that CVD films had graded composition of silicon oxynitride when the film thicknesses were thinner than 200 Å. For example, 100-Å-thick CVD films showed refractive indices of 1.7 $\pm$ 0.06. When compared to these values in that thickness range, the thermal nitride films grown in ammonia plasma seem to be much more stoichiometric and virtually free from oxygen contamination.

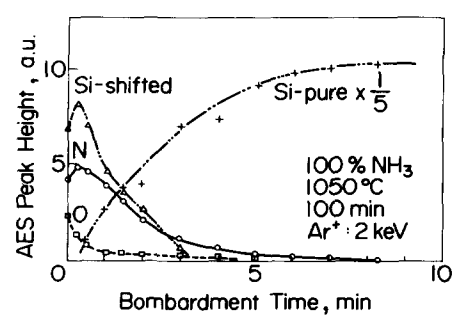

FIG. 3. Auger depth profile of a thermal nitride film grown in rf-activated ammonia gas at 1050 °C for 100 min.

Thermal nitride films grown in ammonia plasma at 1050 °C for 100 min were subjected to analysis by Auger electron spectroscopy (AES). Intense peaks in an AES spectrum were observed at 78 eV for the *LVV* transition of chemically shifted silicon, 264 eV for the *KLL* of carbon, and 498 eV for the *KLL* of oxygen. The carbon peak was that of graphite. The AES depth profile of peak-to-peak width is shown in Fig. 3. The analyzed film was etched step by step by argon ions with an energy of 2 keV which made a sputtering rate of roughly 40 Å/min. The large oxygen fraction observed before the etching may be attributed to adsorptive water because of the rapid decrease for the inner film. The N/O concentration ratio is about 2 at the surface and increases to 11 after etching for the 1 min. The oxygen fraction in thermal nitride films was not greatly influenced by the background pressure and the gas flow rate but slightly increased with the nitridation time. The interface between the nitride film and the silicon substrate is surely believed much steeper than the profile shown in Fig. 3, where knock-on effect by the argon-ion bombardment is not eliminated. Although the profile of the pure silicon is as wide as that in a thermal SiO_2/Si system the authors made, the transition width is not clear at this time.

Etching rates for thermal nitride films measured in a solution of NH_4F:HF = 7:1 at 24 °C are shown in Fig. 4. The etching rate was determined by dividing the initial film thickness by the time required until the etching end. The value decreases rapidly as the nitridation temperture increases above 600 °C, and becomes almost constant above 800 °C; at 1050 °C the etching rate is about 10 Å/min. The value of thermal nitride films grown in nonplasma at 1200 °C is about 30 Å/min, a value comparable to a film grown in ammonia plasma at 800 °C. Considering the etching rate of thermal SiO_2 to be about 1000 Å/min, thermal nitridation certainly occurs to some extent at tempertures below 800 °C. Such films are probably of oxynitride, whose oxygen fraction increases with decreasing nitridation temperature. The origin of the oxygen atoms is thought to be unremoved natural oxide on silicon substrates and oxidant impurities in the ammonia gas. The natural oxide on a silicon surface is removed as volatile species at a temperature above 800 °C. Since oxidation of silicon is thermodynamically much faster than nitridation, it is necessary to reduce the amount of oxidant in the reaction environment. Further, the rf-activated ammonia gas makes the gas more reactive for growing oxygen-free

nitride films. Influences of backstreaming of air while inserting wafers and penetration of oxygen through a quartz tube are avoided in the present system utilizing an rf furnace.

In conclusion, a new procedure for plasma-enhanced thermal nitridation of silicon has been developed. Highly purified ammonia plasma is generated by rf power heating silicon carbide coated carbon susceptors. At a substrate temperture of 1050 °C, thermal nitride films are grown to a thickness greater than 100 Å. These films exhibit properties quite close to stoichiometric Si_3N_4 and are virtually free from oxygen contamination. The growth procedure is easily incorporated into the conventional LSI processing. Practical applications of the thermal nitride films will certainly be enlarged by this technology.

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Light-flash induced metallic silicides from titanium films on silicon

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Reaction of thin titanium films on silicon has been observed in forming polyphase silicides by flash irradiations with full width at half-maximum of 100 μs. Ion back scattering and optical micrographic studies show that the metallization occurs only when the temperature of the metal surface reaches the melting point. The experimental threshold irradiation energy density for the metal surface to reach the melting point is 17.6 J/cm^2, which is close to the theoretical value of 20.4 J/cm^2, based on the strong-thermal-diffusion-limit approach.

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To produce ohmic contacts as electrodes for collecting carriers in semiconductors, one usually applies heat to metal films on silicon to form silicides. For most metals in semiconductors, the diffusivities at high temperatures are very high, and the metal atoms diffuse deeply into the semiconductor forming recombination or trapping centers, so that only a few metals can be used as ohmic contact in the high-temperature heat treatment. Inducing the metal-semiconductor reaction by a short-pulse flash lamp has an advantage of obtaining very small diffusion lengths of impurity metal atoms. There have been some discussions about laser induced reaction of metal films on silicon.[1-3] Previous studies[4] of arc annealing of ion-implanted silicon show that the flash-lamp energy is enough to cause the melting of a silicon surface. In this work we have found that three processes of device fabrication can be completed by a single flash of light. These processes are (i) the recrystallization of the ion-implanted layer, (ii) the depositing of the metal on the silicon from the electrode material by ion bombardment, and (iii) the reaction of the metal film with silicon to form silicide by the light flash.

Titanium films of 600 and 1700 Å were deposited with an electron gun source onto [111], 1–10 Ω cm silicon in a vacuum of 4×10^{-7} Torr. The silicon wafers had been dipped in dilute HF solution prior to the deposition to etch away any oxide layer, so that the metal film and the silicon could have an intimate contact. Metalization processes were performed by locating the sample inside a demountable flash lamp as described in previous work.[4] The electrodes were composed of 50% tungsten and 50% copper with a sparking distance of 3 cm. The wafers were held at a distance of 1.5 cm

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