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## Oxynitridation of silicon by remote-plasma excited nitrogen and oxygen

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Direct oxynitridation of silicon is performed by remote-plasma excited nitrogen and oxygen gaseous mixtures at 550 °C. Nitrogen atoms are mainly incorporated near the SiO<sub>2</sub>–Si interfaces with Auger electron spectroscopy measurements. We have controlled the peak density of nitrogen up to at least several atomic percents, varying the partial pressure of nitrogen and oxygen. The supply of active oxygen species is required for the growth of oxynitride films, but their excess supply reduces the density of nitrogen in the films. The proposed technique is a unique process to obtain high quality ultrathin dielectrics.  $\bigcirc$  1996 American Institute of Physics. [S0003-6951(96)01806-3]

Oxynitride films have been intensively investigated as a high-quality gate dielectric.<sup>1–5</sup> The incorporation of nitrogen at the oxide-silicon interface is considered to improve its dielectric properties, such as a charge to breakdown and immunity to hot carrier injection.<sup>3,4</sup>

Various researchers have reported on the oxynitridation process of silicon with a conventional furnace or a flash lamp reactor in nitrous oxide gas.<sup>4,6</sup> The nitrogen content in the N<sub>2</sub>O grown films is less than a few percent, and the electric properties are not as good as those of the NH<sub>3</sub> nitrided films having several percents of nitrogen.<sup>7</sup> However, the NH<sub>3</sub> nitrided films or deposited films must be annealed or reoxidized at high temperature to remove the Si–H bonds, which is believed to induce electron traps.<sup>8</sup>

A very recent study<sup>9</sup> has proposed a preparation technique of oxynitride silicon films by the exposure of remoteplasma excited  $N_2O$  and the subsequent chemical vapor deposition at low temperature, and has achieved the equivalent films to those by rapid thermal annealing in  $N_2O$ .

In this work, we tried direct oxynitridation of silicon by remote-plasma excited nitrogen and oxygen gaseous mixtures at low substrate temperature. The wide range of nitrogen content can be expected by choosing the appropriate flow-rate condition. After the film growth nitrogen depth profiles in the films were investigated with AES (Auger electron spectroscopy) measurements.

We used the (100) oriented *n*-type single-crystalline silicon substrates with resistivity of  $8-12 \ \Omega$  cm in the experiments. The samples were boiled in an alkali solution of H<sub>2</sub>O:NH<sub>4</sub>OH:H<sub>2</sub>O<sub>2</sub> (6:1:1) for 10 min, and rinsed with flowing DI (de-ionized) water. Then, the samples were dipped into a dilute hydrofluoric acid solution of H<sub>2</sub>O:HF (50:1) for 0.5 min, rinsed with DI water again and blown dry with N<sub>2</sub> gas.

Figure 1 shows a schematic diagram of the experimental system. The substrate was mounted on the susceptor in the cold wall reaction chamber, and the temperature was controlled to 550 °C by a resistive heater. The substrates cannot be nitrided below this temperature without nitrogen plasma.  $N_2$  and  $O_2$  gaseous mixtures were introduced into the reaction chamber at a total flow rate of 600 sccm through the

discharge tube made of quartz with an internal diameter of 11 mm. The total pressure was maintained between 1 and 16 Torr by evacuating with a dry pump. The microwave power (2.45 GHz) of 90 W applied to the discharge tube in TE01 mode, excites and decomposes the nitrogen and oxygen molecules. The distance between the center of the excited region and the substrate was 200 mm. We also carried out experiments by introducing the oxygen gas through the bypass line without the plasma.

In order to investigate the film-growth kinetics, the gas analysis was performed. The intermediate products were introduced into the gas-analysis chamber, which is connected to the reaction chamber, by the differential pumping system through the gas inlet of pinhole with about 0.2 mm diam set near the sample surface. The intermediate species were detected with quadrupole mass analyzer which was mounted in the analysis chamber, where the electron energy for the gas ionization was 20 eV.

The depth profiles of each element in the grown films were investigated with AES measurements, using an argon ion sputtering technique. The sputtered depth was estimated from the sputtering time, where we supposed that the sputtering rate of the samples is as large as that of the thermally grown silicon dioxide films. The composition of each element was determined from the differential intensity of the AES signal.

First, the substrates were oxynitrided by plasma excited nitrogen and bypassed oxygen, where the total pressure and time were 1 Torr and 60 min, respectively. In this condition the grown oxynitride films have a rather high density of nitrogen. The oxynitride films are grown without the plasma



FIG. 1. Schematic diagram of experimental apparatus.

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FIG. 2. Depth profiles of Auger signal intensity for Si, O, and N as a parameter of the ratio of the flow rate of nitrogen with respect to that of oxygen, where the total pressure was 1 Torr and the processing time was 60 min.

excitation for oxygen, because oxygen molecules can react with silicon. The density of nitrogen has a maximum value near the SiO<sub>2</sub>–Si interface, in the same manner as that by the conventional oxynitridation process in N<sub>2</sub>O.<sup>3,4</sup> By varying the ratio of the flow rate of nitrogen with respect to oxygen from 100 to 2, the nitrogen content varies from 15% to 3%. However, the growth rate is very slow in this procedure, where the thickness of the grown films is below 2 nm.

Next, the nitrogen and oxygen gas mixtures were excited by the plasma. Figure 2 shows the depth profiles of Auger signal intensity for Si, O, and N as a parameter of the ratio of the flow rate of nitrogen with respect to oxygen, which corresponds to the partial pressure of nitrogen. The total pressure was 1 Torr and the process time was 60 min. With the excitation of oxygen the thickness of the grown films increases by approximately three times as that without  $O_2$  excitation for the same flow rate condition, but the nitrogen content in the films decreases to a factor of three.

Decreasing the ratio of the flow rate of nitrogen with respect to oxygen, the thickness of the grown film increases, but the nitrogen peak density decreases. These results suggest an adequate correlation between the growth rate and the peak density of nitrogen. The excited oxygen greatly enhances the growth of the films, but decreases the nitrogen content. Considering the sensitivity for each element, the maximum nitrogen content is estimated to be 10% in Fig. 2 for N<sub>2</sub>/O<sub>2</sub>= 380. The value of the nitrogen content may include the measurement error of about 20% of itself in this study.

Figure 3 shows the dependence of the peak density of nitrogen and the thickness of the grown films on the total pressure. The ratio of nitrogen flow rate with respect to that of oxygen was 200 and the oxynitridation time was 60 min. In Fig. 3, by increasing the total pressure, the peak density of nitrogen decreases and the thickness of the film increases. The increase of the growth rate is due to the increased supply of oxidation species.

Now, we discuss a model of the oxynitride growth. We suppose that the silicon atom at the  $SiO_2-Si$  interface would be joined to the two oxygen atoms through the front bonds and two silicon atoms through the back bonds.<sup>10</sup> In the first step of the oxynitride growth, the oxidation species attacks one of the silicon-silicon back bonds at the SiO<sub>2</sub>-Si interface



FIG. 3. Dependence of the peak density of nitrogen and the thickness of the grown films on the total pressure, where the ratio flow rate of nitrogen with respect to that of oxygen was 200 and the processing time was 60 min.

and an oxygen atom is spontaneously inserted between the silicon atoms. Consequently, this oxygen atom likely induces a stress in the remaining silicon-silicon back bond, which should be much larger than that in an equilibrium condition. Then, if the nitrogen atom exists near this site, the nitrogen will easily attack the unstable back bond and incorporate into the lattice.

We have also tried the nitridation of an SiO<sub>2</sub>–Si sample by the remote-plasma excited nitrogen (without oxygen) at 550 °C, where the thickness of the SiO<sub>2</sub> film was about 10 nm. In this experiment, we cannot detect the nitrogen either in the SiO<sub>2</sub> films or at the interfaces with AES measurements. The SiO<sub>2</sub> and the interfaces are hardly nitrided even by the excited nitrogen in the absence of oxygen. Therefore, the oxynitridation process requires both oxidation and nitridation of a silicon atom simultaneously. On the other hand, the excess supply of oxygen species reduces the nitrogen content near the interface by accelerating the film growth. Further investigation of the *in situ* photoelectron analysis should be performed to indicate the validity of the above discussion.

Finally, the thickness and the nitrogen profiles of the grown films have been investigated as a function of the oxynitridation. The thickness of the grown films is proportional to the square root of the oxynitridation time by at least above 2 nm. This result indicates that the oxynitride growth is limited by the diffusion of reactive species, and is consistent with that for the plasma oxidation.<sup>11</sup>

Figure 4 shows the dependence of the nitrogen distribu-



FIG. 4. Dependence of the nitrogen depth profiles on the oxynitridation time, where the ratio of flow rate of nitrogen with respect to that of oxygen was 200 and the total pressure was 1 Torr. The depth of the  $SiO_2$ -Si interface in each sample is also indicated as a dashed line.

tion of the time. Increasing the processing time, the site of the peak moves accompanied by the  $SiO_2$ -Si interface. The reason of the decrease of nitrogen near the surface has not been clear at present.

In order to examine the radicals around the sample surface, the gas analysis was performed for the same experimental condition as that in Fig. 4. The density of the plasmainduced radicals was estimated by substructing the ioncurrent data without the plasma from those with the plasma and supposing the same ionization efficiency for all species. The results show that the atomic nitrogen and atomic oxygen would exist at least 1% and 0.4% in the gas phase, respectively. A similar amount of NO and N<sub>2</sub>O is also observed, but their contribution to the reaction may be less than that of N and O, considering their low reactivity. Analogous to the case of the annealing in N<sub>2</sub>O ambient or in ozone ambient,<sup>12</sup> the decrease of nitrogen near the surface is possibly due to the removal of nitrogen by the atomic oxygen.<sup>12</sup>

On the other hand, the peak density of nitrogen near the interface scarcely depends on the time in Fig. 4. This result indicates that the ratio of the supply of the nitride species with respect to that of oxide species is almost constant and dominates the incorporation of nitrogen into the interface during the film growth in our experiments. This result would support the above discussion for the incorporation process of nitrogen. The behavior on the time gives a possibility to obtain a thick film without decreasing the nitrogen content near the interface.

In summary, we have demonstrated direct oxynitridation of silicon by remote-plasma excited nitrogen and oxygen gaseous mixtures at 550 °C. Nitrogen depth profiles in the grown films were investigated with AES measurements. The density of nitrogen atoms has a peak near the  $SiO_2$ -Si interfaces as that in the films grown in the furnace in N<sub>2</sub>O atmosphere. We easily obtain the hydrogen free oxynitride films containing several atomic percents of nitrogen by the single step process. The proposed technique will give a useful fabrication procedure for highly reliable dielectric films in the future devices, although we have not confirmed the electrical properties of the grown films. Moreover, we have indicated the great influence of the oxygen species on the oxynitride growth and the incorporation of nitrogen in this system.

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