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著者	室田　淳一
journal or publication title	Applied Physics Letters
volume	76
number	3
page range	342-344
year	2000
URL	http://hdl.handle.net/10097/47690

doi: 10.1063/1.125748

Contribution of radicals and ions in atomic-order plasma nitridation of Si

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(Received 24 June 1999; accepted for publication 19 November 1999)

Atomic-order nitridation of Si(100) by an ultraclean electron-cyclotron-resonance nitrogen plasma and contribution of radicals and ions to the nitridation have been investigated. The N atom concentration on Si(100) increases with the plasma exposure time and tends to saturate to a value corresponding to a few atomic layers. In the initial stage, the N atom concentration is normalized by the product of the relative radical density with the nitrogen plasma exposure time and the number of the incident ions is much smaller than the nitridation amount, which means the radical reaction is dominant. Assuming Langmuir-type kinetics neglecting desorption, an excellent agreement is observed by fitting the experimental data. In the saturation region, the N atom concentration is normalized by the number of incident ions and becomes higher than that corresponding to the double atomic layers. Therefore, it is suggested that nitridation of the deeper atoms below the surface is induced by the ion incidence. © *2000 American Institute of Physics.*
[S0003-6951(00)03803-1]

Atomic-order process at low temperatures is necessary to develop ultrasmall Si-based devices made of group IV semiconductors. The atomic-order nitridation at a low temperature is favorable for the future device application, for example, the ultrathin gate insulator, the P or B diffusion barrier,[1] etc. We have reported the atomically controlled process of a Si–N system, such as atomic-order thermal nitridation of Si(100)[2] and atomic-order plasma-role-share etching of Si_3N_4.[3] Plasma processing is extremely useful for enabling lower process temperatures and making use of process gases of low reactivity, e.g., N_2. In plasma processing, it is very important to clarify the contribution of ions and radicals for realization of damage-free nitridation in the atomic order. Recently, there have been a number of attempts to carry out nitridation[1] and deposition[4] of silicon nitride using plasma excitation. However, there have been no report on the contribution of radicals and ions to atomic-order nitridation.

In the present work, the atomic-order plasma nitridation of Si(100) by a nitrogen plasma without substrate heating has been investigated using an ultraclean electron-cyclotron-resonance (ECR) plasma. Based on the comparison of the nitridation characteristics with the relative radical exposure amount and the ion incident flux, the contribution of radicals and ions to atomic-order nitridation is discussed.

Nitridation of the Si(100) surface by a nitrogen plasma was performed without substrate heating using an ultraclean ECR plasma apparatus, schematically shown in Fig. 1.[5,6] The apparatus contains a double load-lock system with a load-lock chamber and a transfer chamber. The ultimate vacuum of the reaction chamber generated by a turbomolecular pumping system is $\sim 7\times 10^{-7}$ Pa. N_2 gas used is of ultraclean grade and is introduced into the ECR plasma-generating chamber. The nitrogen pressure during the process (P_{N_2}) was monitored by a Baratron gauge. Nitrogen plasma was generated for 2–9720 s at 2.56 or 4.40 Pa with the supplied microwave (2.45 GHz) power of 50 or 700 W. The number of the incident ions onto the wafer was controlled by opening and closing the shutter in front of the wafer. The position of the shutter is $\sim$15 mm apart from the wafer surface. When the shutter is closed, the directional incidence of ions is suppressed, and radicals and a part of ions in the nitrogen plasma arrive at the surface from the sideward opening. The optical emission from excited N, N^+, N_2, and N_2^+ was measured by IMUC7000 multichannel spectrometer, and the ion current density was measured by an electrostatic mesh electrode system at the substrate position.[7]

The substrates used were *p*-type mirror polished Si(100) wafers. After cleaning by several cycles in a 4:1 solution of H_2SO_4 and H_2O_2 and in deionized (DI) water, the substrates were treated in 1%–2% HF to remove native oxides on the Si surface and rinsed with DI water just before loading into the load-lock chamber of the ECR apparatus. After nitridation of Si(100), the surface N atom concentration was esti-

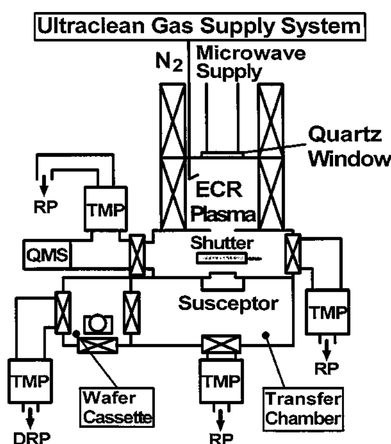

FIG. 1. Schematical diagram of the ultraclean ECR plasma apparatus. N_2 gas is introduced into the plasma-generating chamber. The shutter is $\sim$15 mm apart from the wafer.

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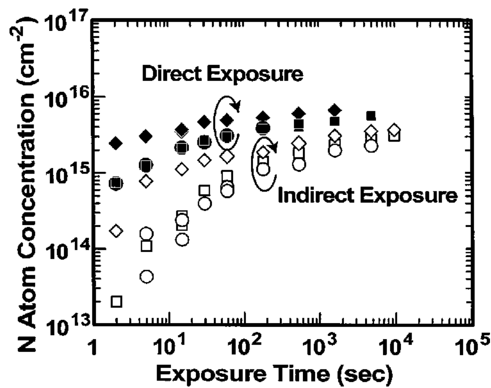

FIG. 2. Dependence of the N atom concentration on the nitrogen plasma exposure time. P_{N_2} and the microwave power are 4.4 Pa and 50 W (○),(●), 2.6 Pa and 50 W (□),(■), and 2.6 Pa and 700 W (◇),(◆) for the indirect (○), (□), (◇) and direct exposure (●),(■),(◆).

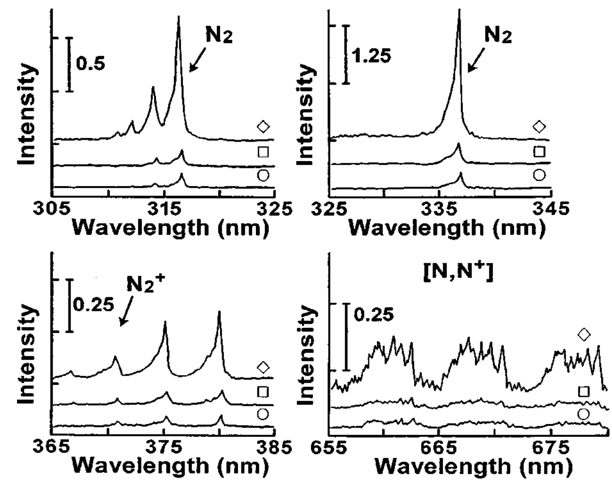

FIG. 3. Optical emission spectra of typical nitrogen species in the nitrogen plasma. P_{N_2} and the microwave power are 4.4 Pa and 50 W (○), 2.6 Pa and 50 W (□), and 2.6 Pa and 700 W (◇).

mated by x-ray photoelectron spectroscopy (XPS).[2]

Figure 2 shows the dependence of the N atom concentration on Si(100) on the nitrogen plasma exposure time under various plasma conditions. The nitridation of Si occurs even without external substrate heating, and the N atom concentration increases with the nitrogen plasma exposure time and tends to saturate to a few atomic layers ($2-6\times10^{15}$ cm^{-2}), although it depends on the microwave power and the N_2 gas pressure. When the shutter is opened (direct exposure), the N atom concentration on Si becomes higher than that with the shutter closed (indirect exposure) at each exposure time. It is noted that radicals and negative ions remaining for a few ms in nitrogen postdischarge plasmas[8] may contribute to the nitridation. However, in the case of the indirect exposure in Fig. 2, the N atom concentration is about 2×10^{13} cm^{-2} at 2 s and increases with the nitrogen plasma exposure time. It is clear that the N atom concentration in the nitrogen post discharge plasma is below 2×10^{13} cm^{-2}. Therefore, the effect of the remaining species on nitridation could be almost neglected in the present experiments, since the almost data shown are above 10^{14} cm^{-2}.

In order to clarify the contribution of radicals and ions to nitridation, it is necessary to compare nitridation characteristics with the relative incident radical density and the incident ion flux. The optical emission from the typical species in the nitrogen plasma is shown in Fig. 3. The optical emission intensity (i_N) depends on the N_2 gas pressure and the microwave power. The change of i_N indicates the change of the number of the excited species in the nitrogen plasma. The dependence of each i_N on the plasma condition for the excitation species such as N_2 (316.5, 337.0 nm), N_2^+ (370.5 nm) and [N, N^+] (655–680 nm) is similar. The relative intensity (I_N) was calculated by comparing the optical emission at each plasma condition with that at 4.4 Pa with the microwave power of 50 W (open circle). I_N becomes 1.3 for the plasma at 2.6 Pa with 50 W (open square) and 8 for the plasma at 2.6 Pa with 700 W (open diamond). Figure 4 shows the dependence of the N atom concentration on the product of the relative optical emission intensity (I_N) and the nitrogen plasma exposure time (t). It is found that the N atom concentration is normalized well by $I_N\times t$ in both the cases of the direct and indirect exposures. Therefore, the radical can be a major species to contribute to the plasma nitridation of Si.

In the indirect and direct exposure, the flux density of the incident ions were 1.0×10^{10} and 5.6×10^{12} cm^{-2} s^{-1} for the plasma at 4.4 Pa with 50 W (open and closed circles), 1.8×10^{11} and 2.5×10^{13} cm^{-2} s^{-1} for the plasma at 2.6 Pa with 50 W (open and closed squares), 3.2×10^{11} and 4.1×10^{13} cm^{-2} s^{-1} for the plasma at 2.6 Pa with 700 W (open and closed diamonds), respectively. These flux densities of the incident ions are much smaller than the N atom concentration per nitridation time in the initial nitridation where the N atom concentration is below about the double atomic layers (1.4×10^{15} cm^{-2}). Furthermore, the N atom concentration was not normalized by the number of the incident ions, as shown below. Therefore, the contribution of ions to nitridation can be neglected in the initial stage of nitridation.

Assuming that the radicals react only with the atoms of the surface and the surface reaction with radicals proceeds according to Langmuir-type kinetics neglecting desorption, the N atom concentration is given by

$$N_N=N_{sat}\times[1-\exp(-k\times\alpha\times I_N\times t)], \quad (1)$$

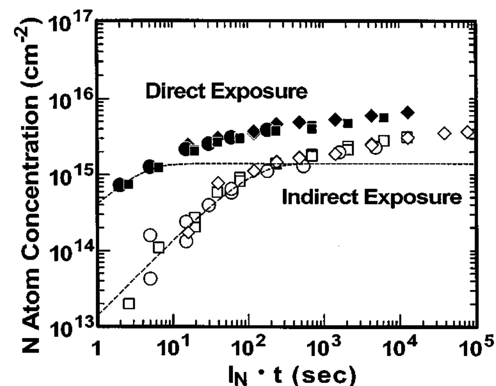

FIG. 4. Dependence of the N atom concentration on the product of the relative optical emission intensity (I_N) and the nitrogen plasma exposure time (t). P_{N_2} and the microwave power are 4.4 Pa and 50 W (○),(●), 2.6 Pa and 50 W (□),(■), and 2.6 Pa and 700 W (◇),(◆) for the indirect (○),(□),(◇) and direct exposure (●),(■),(◆). The broken line shows the values by Eq. (1).

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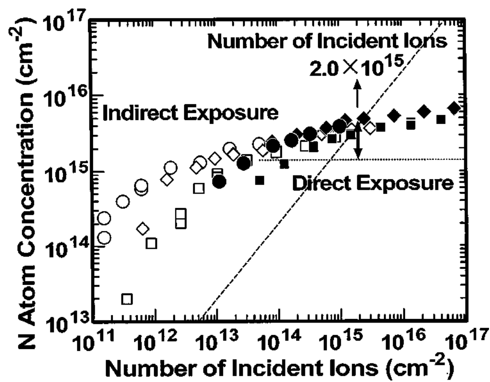

FIG. 5. Dependence of the N atom concentration on the number of the incident ions. P_{N_2} and the microwave power are 4.4 Pa and 50 W (○),(●) 2.6 Pa and 50 W (□),(■), and 2.6 Pa and 700 W (◇),(◆) for the indirect (○),(□),(◇) and direct exposure (●),(■),(◆). The broken line indicates the N atom concentration when all of the incident nitrogen ions contribute to nitridation. The dotted line shows the double atomic layers (1.4×10^{15} cm^{-2}).

where N_{sat} is the saturation N atom concentration, k the reaction rate constant of the radicals, I_N the relative intensity of the emission intensity, α the constant to convert I_N to the number of the incident radicals and t the nitrogen plasma exposure time. The broken line in Fig. 4 is obtained by fitting the experimental data to Eq. (1), where N_{sat} is set 1.4×10^{15} cm^{-2} as in the case of low temperature (400 °C) thermal nitridation of Si.[2] In the indirect exposure, good agreement is observed in the initial nitridation region where the N atom concentration is smaller than 1.4×10^{15} cm^{-2}. However, the N atom concentration in the direct exposure is higher than that in the indirect exposure. This may be caused by the contribution of the ion-induced reaction, the increase of the substrate temperature due to the ion incidence and the change in the incident radical density. In the saturation region, the deviation occurs with further slow nitridation. Even when N_{sat} was set another value corresponding to a few atomic layers, some deviation remained in the saturation region, although a similar fitting for the initial nitridation was obtained within the experimental error. This also indicates that the radicals mainly cause the initial nitridation of Si. On the other hand, the deviation in the saturation region can be due to contribution of the incident ions, because the N atom concentration is higher than that corresponding to the double atomic layers, and because the incident energetic ions are expected to react with the deeper atoms of the surface.

Figure 5 shows the dependence of the N atom concentration on the number of the incident ions. The broken line indicates the N atom concentration if each incident ion contributes to make two N atoms in the nitride. It is found that in the initial nitridation, the N atom concentration does not agree well and is much higher than the broken line. Therefore, it is considered that the radical reaction is dominant in the initial nitridation. In the saturation region, however, the N atom concentration is in the same order of the number of the incident ions and almost the same in both the cases of the direct and indirect exposures when the number of the incident ions was the same, i.e., $\sim2.0\times10^{15}$ cm^{-2}. Therefore, it is suggested that nitridation of the deeper atoms below the surface is induced by the ion incidence.

In conclusion, the N atom concentration on Si(100) increases with the nitrogen plasma exposure time and tends to saturate to a value corresponding to a few atomic layers ($2-6\times10^{15}$ cm^{-2}). In the initial stage, the N atom concentration is normalized by the product of the relative radical density and the plasma exposure time and the number of incident ions is much smaller than the nitridation amount, which means the radical reaction is dominant. Assuming Langmuir-type kinetics neglecting desorption, an excellent agreement is observed by fitting the experimental data. In the saturation region where the N atom concentration becomes higher than that corresponding to the double atomic layers, the N atom concentration is almost the same in both the cases of the direct and indirect exposures when the number of the incident ions is the same. Therefore, it is suggested that nitridation of the deeper atoms below the surface is induced by the ion incidence.

The authors greatly acknowledge Dr. M. Sakuraba for valuable discussions and encouragements throughout this study. This study was partially supported by the Public Participation Program for the Promotion of Information Communications Technology R&D from the Telecommunications Advancement Organization of Japan, JSPS Research for the Future Program (No. JSPS-RFTF97P00202), the Mitsubishi Foundation, a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan, and the Murata Science Foundation.

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