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H. Kobayashi[a)]
PRESTO, Japan Science and Technology Corporation, and Department of Chemistry, Faculty of Engineering Science and Research Center for Photoenergetics of Organic Materials, Osaka University, Toyonaka, Osaka 560, Japan

T. Mizokuro and Y. Nakato
Department of Chemistry, Faculty of Engineering Science and Research Center for Photoenergetics of Organic Materials, Osaka University, Toyonaka, Osaka 560, Japan

K. Yoneda
ULSI Process Technology Development Center, Matsushita Electronics Corporation, 19 Nishikujo-Kasugacho, Minami-ku, Kyoto 601, Japan

Y. Todokoro
Research Planning Department, Corporate Research Division, Matsushita Electric Industrial Co., Ltd., 3-1-1, Yagumo-Nakamachi, Moriguchi, Osaka 570, Japan

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Low temperature nitridation of silicon oxide layers by nitrogen plasma generated by electron impact is investigated using x-ray photoelectron spectroscopy (XPS) and synchrotron radiation ultraviolet photoelectron spectroscopy and it is found that a large amount of nitrogen can be incorporated in the layers. The valence band structure of the oxide surface nitrided at 25 °C is similar to that of Si_3N_4, while that nitrided at 700 °C resembles the mixture of silicon oxide and silicon oxynitride. Measurements of XPS depth profiles show that the nitrogen concentration is high near the surface and the oxide/Si interface. © *1997 American Institute of Physics.* [S0003-6951(97)02340-1]

Silicon oxynitride is a good candidate for better gate dielectrics than SiO_2. It acts as a good barrier to boron penetration,[1,2] and has good interface properties, such as low interface state density, strength for hot carrier injection, and charge to breakdown, etc.[3–5] Incorporation of nitrogen in oxide layers can be achieved by oxidation of Si in N_2O (Refs. 1, 3, 4, 6–8) or NO (Refs. 7, 9, 10) atmospheres. In the case of N_2O, the amount of nitrogen atoms incorporated is less than a few atomic percent[1,6–8] and thus, the characteristics are not greatly improved. In the case of NO, a relatively high amount of nitrogen can be incorporated, but the reaction is self-limiting, resulting in thin layers.[7,9] Moreover, the reaction of Si with N_2O or NO proceeds only at high temperatures above 900 °C. Nitridation using NH_3 occurs at lower temperatures, and a high amount of nitrogen can be introduced in the oxide films. However, a high amount of hydrogen, which acts as electron traps,[11] is also incorporated, and its removal requires high temperature heat treatments.

Silicon dioxide layers can be nitrided at low temperatures using plasma technique, and reasonably good electrical characteristics are achieved.[2,5,12] In the case of NH_3 plasma, however, the formation of electron traps due to incorporated hydrogen cannot also be avoided.[2,5] Using nitrogen plasma, on the other hand, the amount of introduced nitrogen is very low,[5] or even lower than the detection limit of Auger electron spectroscopy.[13]

In the present study, nitridation of silicon dioxide layers is performed at temperatures below 700 °C using nitrogen plasma generated by electron impact, and it is found that a high amount of nitrogen can be incorporated in the oxide layers.

After cleaning boron-doped p-Si(100) wafers of 10∼15 Ω cm resistivity using the RCA method, a 6-nm-thick silicon dioxide layer was formed by oxidation at 850 °C for 12 min in oxygen plus hydrogen with the flow rates of 12 and 2 l min^{-1}, respectively. Then, the specimens were introduced into an ultra high vacuum (UHV) chamber for nitrogen plasma treatments and x-ray photoelectron spectroscopy (XPS) measurements.

For the generation of nitrogen plasma, a tungsten filament was heated at 1400 °C in a 1.5×10^{-2} Torr nitrogen atmosphere, and 53 V was applied between the filament and the grid. It was confirmed that nitridation occurred at 23 V applied to the grid with respect to the filament but the nitrogen concentration reduced considerably. In order to avoid the plasma damage due to the charge-up effect,[14] an appropriate bias voltage was applied between the grid and the Si sample, unless otherwise mentioned, so that no current was detected at the sample position.

XPS spectra were measured using a VG SCIENTIFIC ESCALAB 220i-XL spectrometer with a monochromatized Al Kα radiation source. The take-off angle, θ_t, was either 90° (surface-normal direction) or 30°. The p-type substrate Si $2p_{3/2}$ peak was taken as the energy reference (98.3 eV). Depth profile measurements were performed by 2 keV Ar^+ ion etching, followed by the XPS measurements.

Synchrotron radiation ultraviolet photoelectron spectroscopy (UPS) spectra were measured using the BL-3B beamline at the National Laboratory for High Energy Physics.

Figure 1 shows XPS spectra for the silicon dioxide layers nitrided with nitrogen plasma generated by low energy

[a)]Author to whom all correspondence should be addressed. Electronic mail: kobayasi@chem.es.osaka-u.ac.jp

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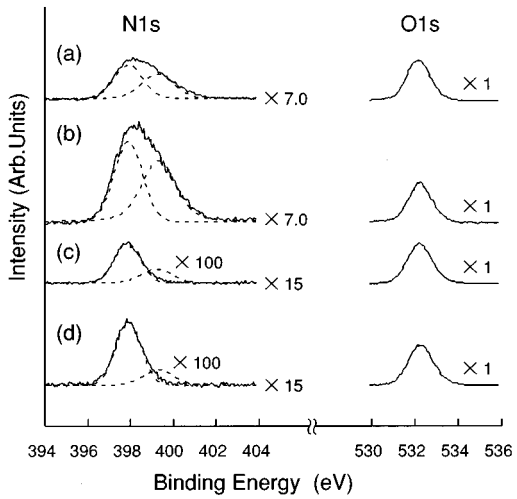

FIG. 1. XPS spectra in the N 1*s* and O 1*s* regions for the silicon oxide layers nitrided with nitrogen plasma generated by electron impact. The nitridation temperature, T_n, and the take-off angle, θ_t, are: (a) $T_n = 25$ °C and $\theta_t = 90$ °; (b) $T_n = 25$ °C and $\theta_t = 30$ °; (c) $T_n = 700$ °C and $\theta_t = 90$ °; (d) $T_n = 700$ °C and $\theta_t = 30$ °.

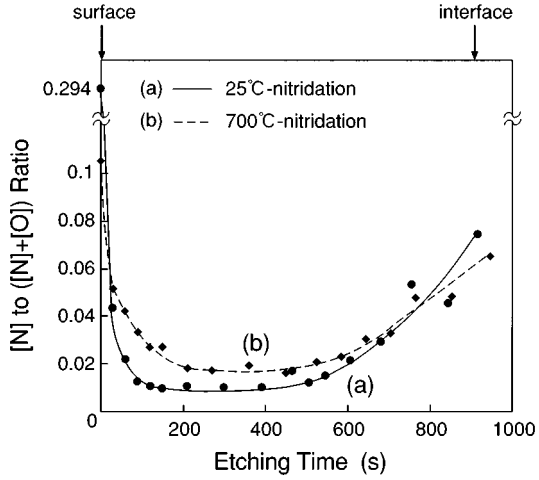

FIG. 2. Depth profiles of the nitrogen concentration ratio, N/(N+O), for the silicon oxide layers nitrided with nitrogen plasma at the following temperatures: (a) 25 °C; (b) 700 °C.

electron impact. In the case of nitridation at 25 °C, a broad peak was observed in the N 1*s* region and resolved into a main peak centered at 397.9 eV and a weaker peak at 399.2 eV [spectra (a) and (b)]. From the N 1*s* binding energy, the main peak is attributed to N atoms with which three Si atoms are bound each in the planar structure, $N{\equiv}Si_3$.[7,8,10,15] The attribution of the weaker peak is more difficult, but it is tentatively attributed to unstoichiometric silicon nitride. It is reported that the binding energy of the N 1*s* peak for SiN_x species varies by ~1.2 eV depending on x.[16] Nitrogen atoms bound to oxygen atoms, N–O, are excluded because the N 1*s* binding energy of this species is much higher, i.e., 401~402.6 eV.[10,15]

For the silicon dioxide layers nitrided at 700 °C, the intensity of the peak due to the unstoichiometric species became much lower [spectra (c) and (d)]. This may indicate that unstoichiometric species probably formed by the replacement of oxygen atoms in the oxide layer to nitrogen atoms is a precursor state of $N{\equiv}Si_3$.

From synchrotron radiation UPS measurements, it is concluded that nitride and oxynitride are formed on the surface after nitridation at 25 and 700 °C, respectively, as described later. However, the main N 1*s* peak for both phases was present at 397.9 eV. This is because nitrogen atoms in both species are bound to three Si atoms each, i.e., $N{\equiv}Si_3$, and only the second nearest neighbor atoms are different.[17] In fact, theoretical calculations show that the partial charge on a nitrogen atom in silicon nitride is $-1.89e$ (e: elementary charge) for α-Si_3N_4 and $-1.87e$ for β-Si_3N_4, almost the same as that for silicon oxynitride of $-1.90e$.[17]

From the ratio of the areal intensity of the N 1*s* peak to that of the O 1*s* peak, the N/(N+O) atomic ratios for the oxide layers in the surface region, i.e., in the range of the photoelectron mean free path of ~3 nm,[18] nitrided at 25 and 700 °C, are estimated to be 29% and 11%, respectively. These nitrogen concentrations are much higher than those incorporated by Si oxidation in N_2O or NO.[1,6–8,10]

The intensity of the N 1*s* peak with respect to that of the O 1*s* peak for the take-off angle, θ_t, of 30° [spectra (b) and (d)] is larger than that for $\theta_t = 90°$ [spectra (a) and (c)], indicating that the nitrogen concentration is high in the surface region.

Figure 2 shows the depth profiles of the nitrogen concentration ratio, N/(N+O), for the silicon oxide layers nitrided at 25 °C [plot (a)] and 700 °C [plot (b)]. For both the nitrided layers, the nitrogen concentration was high at the surface and near the interface. The surface nitrogen concentration for 25 °C nitridation was much higher than that for 700 °C nitridation, whereas the bulk concentration for the 25 °C nitridation was slightly lower than that for the 700 °C nitridation.

The concentration of oxygen atoms which have a mass number similar to that of nitrogen atoms decreased near the interface. This result demonstrates that the increase in the nitrogen concentration near the interface was not caused by the knock-on effect due to ion sputtering. The depth profiles with the high nitrogen concentration at the surface and near the interface were confirmed by etch-back experiments.

The observed nitrogen profiles are preferable to gate dielectrics, because nitrogen atoms in the surface region act as a resistance to boron diffusion[1,2] and those in the interface region improve the electrical characteristics.[3–5] Such ideal nitrogen profiles have been produced using NH_3 plasma,[5,12] but have not been achieved using nitrogen plasma.[5,13] This may indicate that nitrogen plasma generated by electron impact possesses different nature from rf plasma, e.g., different composition. By applying a negative bias voltage of −20 V to the sample with respect to the grid, the amount of incorporated nitrogen was increased considerably. This may indicate that positive ions such as N^+ and N_2^+ in the nitrogen plasma play an important role in the nitridation.

Figure 3 shows synchrotron radiation UPS spectra for the silicon oxide layers nitrided by nitrogen plasma. For the surface nitrided at 25 °C [spectrum (a)], peaks were observed at 5.3, 7.6, 10.4, and 20.0 eV. These energies are in good agreement with those observed for stoichiometric Si_3N_4,[19,20] as indicated by the arrows, and they are attributed to the N

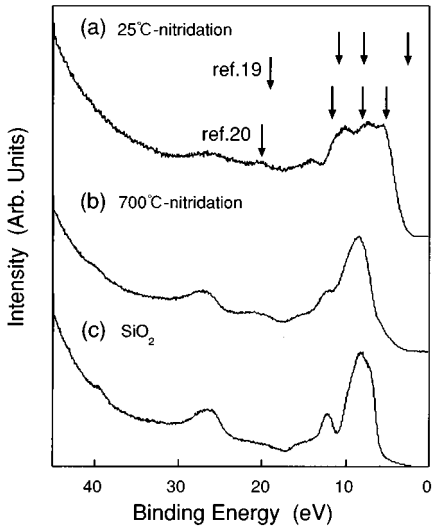

FIG. 3. Synchrotron radiation UPS spectra for the silicon oxide layers nitrided with nitrogen plasma measured at $h\nu = 65$ eV. The nitridation temperature is (a) 25 °C; (b) 700 °C. The spectrum of the silicon oxide layer is included for comparison [spectrum (c)].

$2p_z$ nonbonding state, N $2p$ + Si $3p$, N $2p$ + Si $3s$, and N $2s$, respectively.[21] Therefore, it can be concluded that the SiO_2 surface region of depth in the range of the photoelectron mean free path, i.e., 0.6–0.7 nm,[22] is transformed into Si_3N_4.

By nitridation at 700 °C [spectrum (b)], the spectral feature below 15 eV was slightly broadened, and a new peak due to the N $2s$ level appeared at ~20 eV, but the peak due to the O $2p_z$ nonbonding orbital was present at almost the same position of 8.5 eV as that before the nitridation [spectrum (c)]. It is reported that the O $2p_z$ peak shows a continuous downward energy shift with an increase in the nitrogen concentration of silicon oxynitride.[23] The unchanged O $2p_z$ peak energy indicates that only a small amount of nitrogen is included in the surface region. Therefore, it is inferred that Si atoms to which nitrogen atoms are bonded also are bound to oxygen atoms, i.e., oxynitride.[17]

It is clearly shown that nitridation of the silicon oxide surface proceeds even at 25 °C. Therefore, it can be concluded that the surface reaction is not the rate-determining step. It is also expected that the reaction at the interface occurs easily once the reacting species reaches the interface, because the activation energy for nitridation of Si is likely to be lower than that of SiO_2 due to the much smaller Si–Si bond energy (1.8 eV) than the Si–O bond energy (6.4 eV). Therefore, the diffusion of the reacting species through the oxide layer is most likely to be the rate-determining step.

In summary, silicon oxide layers can be nitrided easily below 700 °C using nitrogen plasma generated by electron impact and a large amount of nitrogen can be incorporated in the layers. The nitrogen concentration is high at the surface and near the interface. For nitridation at 25 °C, the surface region is transformed to Si_3N_4 almost completely, while for nitridation at 700 °C, silicon oxynitride is formed.

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