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Nitrogen incorporation in thin oxides by constant current N_2O plasma anodization of silicon and N_2 plasma nitridation of silicon oxides

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A helical resonator plasma source was used to perform constant current N_2O plasma anodization of silicon and N_2 plasma nitridation of silicon oxides. The nitrogen bonding structure and distribution in the oxides were studied using angle resolved x-ray photoelectron spectroscopy. Nitrogen corresponding to a $N\text{–}Si_3$ bonding structure was detected at the silicon side of the interface, the $Si\text{–}SiO_2$ interfacial region, and the bulk oxide in a 4.5 nm N_2O plasma grown oxide. The distribution profile of nitrogen in the oxide, determined from a normalized N $1s$/Si $2p$(ox) ratio, showed a continuous decrease from the silicon side of the interface towards the bulk oxide. Also, strong nitrogen peaks corresponding to either a $N\text{–}Si_3$ or a $N\text{–}Si_2$ bonding structure were detected throughout a 9.1 nm O_2 plasma grown oxide after postanodization constant current N_2 plasma nitridation. © *1996 American Institute of Physics.* [S0003-6951(96)01834-7]

As device dimensions shrink below 0.35 μm, the electric fields across thin gate dielectrics continue to increase, and reliability problems become severe. As a result, the superior electrical properties exhibited by oxides with nitrogen incorporation, such as higher dielectric breakdown values,[1,2] reduced interface state generation,[3] improved $I-V$ and $C-V$ characteristics;[4] and increased resistance to boron diffusion from doped-polysilicon gates[5] have led to an interest in the development of nitrided oxides as alternatives to SiO_2 for gate dielectrics.

Furnace,[2,3,6,7] RTP (rapid thermal processing),[3–5,8–10] and downstream plasmas[11,12] have been used for nitrogen incorporation in gate oxides using either N_2O (nitrous oxide),[3,9–11] NO (nitric oxide)[4,6] or mixtures of N_2 and O_2.[2,11] In general, RTP oxides display nitrogen accumulation at the $Si\text{–}SiO_2$ interface,[3] thermal oxides display either nitrogen peaked at the interface[6,7] or a roughly uniform nitrogen distribution throughout the oxide,[2] and plasma-grown oxides have nitrogen at the $Si\text{–}SiO_2$ interface[11] or at the SiO_2 surface.[12] Variation exists in the nitrogen-bonding structure reported even within the same kind of process, ranging from $N\text{–}(Si_3)$[3] to Si–O–N.[5] The bonding structure, distribution, and quantity of nitrogen incorporated are clearly dependent on the growth process and conditions used. Comparatively less information is available on the individual effects of bonding structure, distribution and quantity of nitrogen on electrical properties, but a strong dependence is likely. For example, a higher quantity of nitrogen at the $Si\text{–}SiO_2$ interface increases boron diffusion resistance[5] and reduces interface state generation;[3] the N–O bond may play a large role in determining immunity to interface state generation.[10] To realize fully the potential of nitrided oxides, an understanding, as well as optimization and control of the bonding structures that occur in nitrided oxides is needed.

Plasma oxidation offers a possible alternative to high temperature oxidation.[13] In our work, we use a helical resonator plasma source[14,15] for constant current N_2O plasma anodization of silicon and N_2 plasma nitridation of silicon oxides. Preliminary results indicate that the current driven process has the potential of incorporating relatively high concentrations of nitrogen into the oxide. To our knowledge, this is the first demonstration of single crystal silicon anodization in N_2O and silicon oxide nitridation in N_2 at low temperature. Also, the current driven processes permit control of nitrogen incorporation at temperatures below 400 °C.

The silicon wafers were (100) p-type with a resistivity of 15–30 Ω cm. They were cleaned using a standard RCA clean and given a (1%)HF dip followed by a DI water rinse and N_2 dry before introduction into the helical resonator reactor. N_2O plasma anodization of silicon was performed at 350 °C, 30 mtorr, 300 W rf forward power and a constant current of 3.8 mA/cm^2. Electron density and electron temperature values measured using a Langmuir probe at these conditions were $\approx 1\text{–}2 \times 10^{10}/cm^3$ and 3–4 eV, respectively. The substrate holder was covered with quartz except for a 50 mm diam circular area, where oxidation occurred.[16] Angle resolved x-ray photoelectron spectroscopy (ARXPS) was performed using a Scienta ESCA-300 spectrometer. The Scienta ESCA-300 combines a rotating Al anode with a monochromator to provide an intense source of monochromatic photons at 1486.6 eV and has a fixed 300-mm mean radius hemispherical analyzer with multichannel detection at the exit plane. These factors contribute to give high signal to noise ratio and high resolution. Also, the product of the x-ray flux and the analyzed area remains approximately constant as the sample is inclined, so the decrease in photoelectron counts with sample tilt is reduced significantly. This allows accurate nitrogen-bonding identification and nitrogen-distribution determination throughout the oxide by ARXPS. Take-off angles of 90°, 45°, 30° and 15° were used in order to obtain penetration depths (vertical depths sampled) of approximately d, 0.7d, 0.5d, and 0.26d where $d=3\lambda$, where λ is the attenuation length of the emerging electron. For example, for a value of $\lambda \approx 3$ nm for silicon in SiO_2,[17] penetration depths of 9, 7, 5, and 2.6 nm can be obtained. All binding energies were calibrated to the adventitious carbon peak at 284.8 ± 0.2. Atomic percentage values were derived from atomic concentrations, which were in turn calculated from the XPS peak intensities and atomic sensitivity factors. Ox-

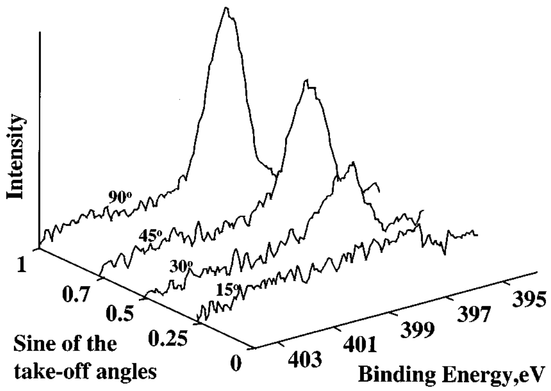

FIG. 1. ARXPS N 1*s* spectra at various take-off angles of a 4.5 nm oxide grown by N_2O plasma anodization of silicon. The peaks at 397.5±0.2 eV are due to nitrogen from a N–Si_3 bonding structure.

ide thicknesses were measured via ellipsometry using a refractive index of 1.465.

Figure 1 shows N 1*s* spectra of a 4.5 nm oxide grown in a N_2O plasma for 1 min. Distinct N 1*s* peaks at a binding energy of 397.5±0.2 eV are evident at take-off angles of 90°, 45°, and 30°. At a 15° take-off angle, the N 1*s* peak at 397.5 eV is very weak. These peak locations are close to the binding energy value reported for the Si–N bond in Si_3N_4; binding energy values for N 1*s* in silicon nitrides vary from 397.5 eV to 397.99 eV.[6,10,18,19] Thus, nitrogen from a N–Si_3 bonding structure can be detected at take-off angles corresponding to penetration depths ranging from the silicon side of the interface to the Si–SiO_2 interface, and is faintly visible in the bulk of the oxide. Intensities of the N 1*s* peaks decrease with take-off angle; this decrease is due to both a small decrease in photoelectron counts and a change in nitrogen concentration.

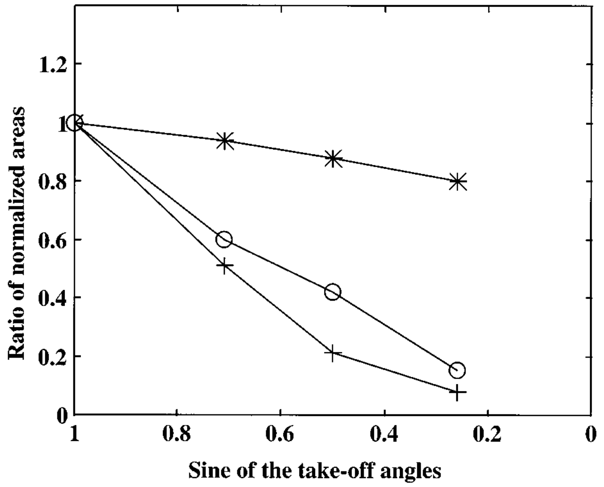

FIG. 2. Normalized distribution ratios of O 1*s*/Si 2*p*(ox), '-*-', Si 2*p*(Si)/Si 2*p*(ox), '-+-', and N 1*s*/Si 2*p*(ox), '-o-', as a function of the sine of the take-off angles in a 4.5 nm oxide grown by N_2O plasma anodization of silicon.

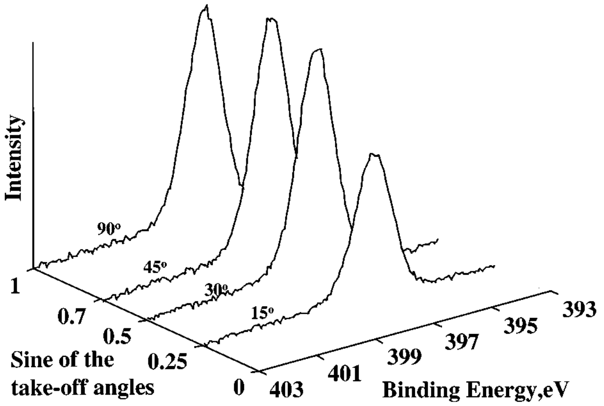

FIG. 3. ARXPS N 1*s* spectra at various take-off angles of a 9.1 nm O_2 plasma grown SiO_2 sample with subsequent N_2 plasma constant current nitridation. The peaks at 398.15±0.2 eV are due to nitrogen either from a N–Si_3 bonding structure or, from a N–Si_2 bonding structure.

Figure 2 shows oxygen, nitrogen, and silicon distribution profiles derived from ARXPS spectra of the 4.5 nm N_2O oxide. The areas under the peaks of N 1*s*, O 1*s*, and Si 2*p*(Si) signals are normalized to that of the Si 2*p* signal from the oxide. This procedure cancels the small difference in photoelectron counts caused by inclination of the sample. Also, all areas have been normalized to those at 90° for each XPS peak for easy comparison.[19] Figure 2 shows that with decreasing take-off angle, the ratio O 1*s*/Si 2*p*(ox) drops only slightly, while the ratio Si 2*p*(Si)/Si 2*p*(ox) decreases substantially, as expected. The N 1*s*/Si 2*p*(ox) ratio also decreases with decreasing take-off angle; the ratio is highest at the largest penetration depth where the silicon side of the interface along with the oxide is sampled. This trend indicates that the nitrogen content decreases from the silicon side of the interface to the SiO_2 surface. Nitrogen atomic percentage values decreased from ≈ 0.7% at 90° to ≈0.2% at 15°.

In order to investigate if the Si_3N_4 formation is due to operation in the constant current mode which would drive negative nitrogen species towards the positively biased silicon, an oxide was grown in a pure O_2 plasma for 3 min to a thickness of 8.6 nm. A N_2 plasma was then used to establish a constant current of 0.75 mA/cm^2 at 50 W rf power and 350 °C for 5 min. The final oxide thickness was 9.1 nm. Figure 3 shows the ARXPS spectra of the oxygen grown, nitrogen current driven oxide. One strong N 1*s* peak at 398.15±0.2 eV is detected at all take-off angles; the nitrogen atomic percentage values obtained were high, ≈5%–8%. This binding energy value is close to that observed for the Si–N bond in Si_3N_4;[6,10,18,19] but is 0.65±0.4 eV higher the N 1*s* binding energy in Fig. 1. This difference may result from a N–Si_2 bonding structure, with the remaining bond to nitrogen being hydrogen or a dangling bond, as suggested from the estimated binding energy shift of −0.5 eV per N–Si bond in Si nitrides.[3] Thus, the observed N 1*s* peak at 398.15 ±0.2 corresponds to either a N–Si_3 or a N–Si_2 bonding structure. At this point, conclusive assignment of this peak to one of the two bonding structures is not possible.

N_2O plasma anodization of silicon results in the rapid formation of a Si_3N_4 bonding structure at the Si–SiO_2 interfacial region. It is likely that some of the nitrogen is replaced by oxygen as the oxide grows. Apparently, the Si_3N_4 structure can be stabilized in the vicinity of the interface during anodization. Such conclusions explain the observed N 1s/

Si 2p(ox) ratio increase with penetration depth. At the same time, nitrogen is not completely replaced by oxygen in the bulk of the oxide; at a 15° take-off angle, the N 1s peak is weak but detectable ($\approx$0.2 at.%). The relatively low temperature used in this work as compared to RTP and furnace grown oxides is likely responsible for the presence of nitrogen in the bulk oxide. It is interesting to note that nitridation occurs on the silicon side of the interface, probably as a result of using constant current. Previously, this phenomenon has been observed only during NO furnace oxidation at high temperature and is believed to be the reason for the improved electrical properties of NO grown oxides.[4,6] Thermal oxidation in our reactor in N_2O under the same conditions for 5 min yields an oxide thickness of 1.1 nm, confirming that the oxide grown by N_2O plasma anodization results from plasma anodization.

We believe that the Si_3N_4 formation is a result of nitridation under constant current conditions. Nitrogen moieties adsorbed on the substrate surface can form negative nitrogen species upon collision with electrons from the discharge, which in turn can be driven towards the positively biased silicon to form silicon nitride. N≡N and N–O have bond energies of 9.83 and 1.7 eV, respectively; with an average plasma electron energy of 3–4 eV, it is likely that a greater fraction of the nitrogen species exist as N_2 in either N_2O or N_2 plasmas. Formation of N_2^- at the substrate can then occur upon collision with electrons.

XPS analysis of a pure O_2 plasma grown oxide shows no nitrogen. Thus, the N 1s peaks in Fig. 3 must arise from the N_2 plasma treatment, specifically as a result of postanodization N_2 current nitridation. The N 1s peak intensity is strong at all take-off angles, indicating that nitrogen is distributed throughout the interfacial region as well as the bulk oxide. This distribution probably results from the fact that extensive oxidation/anodization does not take place when a nitrogen plasma is used for nitridation; therefore, nitrogen is not replaced by oxygen in the bulk oxide nor at the interface. The atomic percentage of nitrogen for the O_2 plasma grown and subsequent N_2 plasma nitrided oxide is higher than that obtained from an oxide of equal thickness grown by N_2O plasma anodization. Higher quantities of nitrogen can therefore be incorporated by establishing a nitrogen current in the absence of oxidizing species.

In conclusion, N_2O plasma anodization results in nitrogen incorporation in the oxide in the form of a Si_3N_4 bonding structure. Some of the nitrogen is replaced by oxygen as the oxide thickness increases. Nitrogen incorporation is a direct result of the current driven process. These constant current processes demonstrate the ability to incorporate nitrogen in thin oxides as $N-Si_3$, which exists primarily at the silicon side of the $Si-SiO_2$ interface using N_2O anodization, and as either $N-Si_3$ or $N-Si_2$, which is present throughout the oxide using post N_2 nitridation. ARXPS analysis of oxynitrides grown for longer times are under investigation; preliminary results indicate the formation of Si-oxynitrides (Si–O–N) in the bulk oxide.

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