The removal of nitrogen during boron indiffusion in silicon gate oxynitrides

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The effect which nitrogen has upon boron diffusion through oxynitride gate dielectrics has been studied with secondary ion mass spectroscopy of polycrystalline silicon–oxynitride–silicon structures, and with x-ray photoelectron spectroscopy of silicon–boron–oxynitride–silicon structures. These studies show that the indiffusion of boron results in removal of nitrogen from the oxynitride. This indicates that the role of nitrogen in suppressing boron penetration is chemical in nature rather than diffusive. © 1996 American Institute of Physics. [S0003-6951(96)02330-3]

As gate oxide dimensions in metal-oxide-silicon field effect transistors (MOSFETs) continue to shrink, the issue of boron diffusion from the polycrystalline silicon gate to the Si channel in p MOSFETs is becoming increasingly important.1 In the past, boron penetration has not been a major problem, due simply to the low diffusivity of B in the gate SiO2, as compared to Si.2 However, the need for thinner gate oxides3 threatens to render gate oxides ineffective as barrier against boron. One solution is to lower the thermal budget subsequent to gate formation. Alternatively, manipulating the crystalline structure of the polycrystalline silicon gate can be somewhat effective in suppressing boron penetration.4 However, one of the most effective approaches, and yet the least understood, is the introduction of nitrogen into the gate oxide. Several methods of nitrogen introduction have been found to be efficacious: plasma NH3 nitridation,5 thermal NH3 nitridation,6 partial growth in NO6 and N2O oxynitridation.7

Understanding the mechanism by which nitrogen inhibits boron indiffusion is an important step in developing optimally robust oxynitrides. The most enlightening work to date was performed by Aoyama et al.,2 who experimentally determined the diffusivity in reoxidized silicon nitride. Mathiot et al.,5 also attempted to quantify the effect of nitridation on the diffusivity of boron using a plasma NH3 nitridation process. Both of these experiments relied upon measurements of the boron concentration in the silicon substrate to calculate an effective diffusivity in the oxide. We present evidence that the mechanism by which nitrogen suppresses boron penetration is chemical rather than diffusive. This is based on our observation of a reaction during indiffusion between boron and nitrogen, resulting in a loss of nitrogen. If this represents a chemical interaction between boron and nitrogen, it suggests that the critical factor in suppressing boron penetration is the probability of boron encountering a nitrogen site. Additionally, the loss of boron presumably results in the creation of an oxide defect. Since the substrateoxide interface is more sensitive to such defects, this leads to the conclusion that the most effective barrier against boron would be a wall of nitrogen at the oxide-polycrystalline silicon interface.

We observed the reaction between nitrogen and boron in two fundamentally different types of samples. Our approach in both cases was to submit oxynitrides to high doses of boron, so that the flux density of boron through the oxynitride approached or exceeded the areal density of nitrogen, and to measure the nitrogen and boron profile with either secondary ion mass spectroscopy (SIMS) or x-ray photoelectron spectroscopy (XPS). The first type of sample was a standard polycrystalline silicon–oxynitride–silicon structure common in MOSFETs. To obtain sufficiently high concentrations of boron in the oxynitride layer for SIMS observation, the low boron density in the polycrystalline silicon of these samples required high annealing temperatures, at least 1000 °C, and annealing times of several hours. The second type of sample was a bilayer silicon–boron structure, evaporated on top of a standard oxynitride. These samples had a much higher boron density, and therefore could be examined with XPS after annealing at temperatures as low as 900 °C. It is important to recognize that boron doses as high as we achieved would be catastrophic to any device. However, this technique was necessary for this investigation, since at boron flux densities realistic for devices, we would not be able to detect alterations to the incorporated nitrogen.

We grew the oxynitrides for the low boron density samples with a four-step furnace process at 900 °C: 5 min O2, 30 min N2O, 30 min O2, and finally 30 min N2O. The flow rate of each gas was 4 SLM (standard liters per minute) in a 3 in. wafer furnace. This produced oxides with a bimodal nitrogen distribution, with one nitrogen peak at the oxide-substrate interface, and another peak 100 Å from that interface. The total oxynitride thickness was 140 Å. Detailed information on these oxides, as well as accurate N depth profiles, has been published previously.7 The low pressure chemical vapor deposited (LPCVD) polycrystalline silicon on top of the oxide was doped in situ with B to a concentration of ~7 × 1019 atoms/cm3, and grown to a thickness of 2000 Å. For the activation anneal of an actual device, we would typically have deposited several hundred angstroms of SiO2 on top of the polycrystalline silicon to trap the B. However, we chose to skip this step, since additional layers would have decreased the effective resolution of the subsequent SIMS analysis by introducing thickness inhomogeneities. As a result we observed a gradual loss of B from the polycrystalline silicon for the higher temperature anneals, although this loss does not qualitatively effect our results. To drive the boron into the oxynitride, we annealed the samples in a MOS furnace in a N2 ambient, and used SIMS to obtain nitrogen and boron depth profiles. The detection threshold for B was 3 × 1017 cm−3, while for N it was better than 1017 cm−3. To locate the oxide layer, we also simultaneously analyzed Si and O concentrations.
The profiles based on the SIMS O2 signal. For the profiles in the boron profiles from the two higher temperature anneals, the concentration in the oxide was in some places higher than the concentration in the polycrystalline silicon. This is a result of the difference in chemical potential of the two materials, giving rise to boron segregation at the interface. The small boron peak in the 1050 °C anneal, located at the nitrogen-rich region near the substrate-oxide interface, cannot be attributed to segregation, and may represent the pileup of boron. This could have been caused by a region of lower diffusivity, or by the pinning of boron by either the incorporated nitrogen or a vacancy caused by nitrogen removal. The effect of the boron influx in causing the nitrogen loss suggests, although it does not prove, that the latter mechanism is responsible.

We also studied a series of high boron density samples, using a 63 Å oxide grown under pure N2O for 30 min at 900 °C. On top of the oxide, we e-beam evaporated 10 Å of boron, followed by a 100 Å cap of silicon. To drive the boron into the oxide we annealed the samples in N2 at various temperatures. Because of the high B levels near the oxide, these samples allowed much lower annealing temperatures than the SIMS samples. We were also able to use XPS to profile for boron and nitrogen. Although the ultimate detection limit for XPS is lower than SIMS, the depth resolution was superior, and provided information on the chemical state of the atoms. To prepare the samples for XPS measurements, we stripped the silicon cap using an aqueous solution of 10% HNO3 and 0.5% HF. To remove the remaining continuous boron film, we immered the sample in hot (130–150 °C) concentrated H2SO4 for 1–2 h. The result was an exposed oxide layer which we profiled using the XPS sputter process described elsewhere.

Figure 2 shows the result of an anneal at 900 °C for 70 min. For comparison, we have also plotted in Fig. 2 the N profile from an unannealed sample. The difference between the two N profiles indicated a 30% loss of N from the oxide. We observed a single boron peak at a binding energy of 186 eV, and we calculated the B profile using the same method with which we obtained the N profile. The profile, shown in Fig. 2, indicated that B had just started to penetrate the oxide at a distance of 30 Å from the oxide-substrate interface, ~50% of the nitrogen was removed, while at 10 Å only 30% of the nitrogen was removed.

In conclusion, we observed the removal of nitrogen in gate oxynitrides as a result of boron indiffusion in two types of samples, using different methods of analysis. Both the low and high boron density samples exhibit a similar behavior: as sufficient quantities of boron penetrate the oxide, a reaction occurs which results in the removal of nitrogen from the oxynitride. This process can occur at temperatures as low as 900 °C, making it an issue during device processing. Prior-
ous works have established that nitrogen incorporation effectively impedes boron indiffusion in gate oxynitrides. Our observation of N loss due to the boron influx suggests that the impeding mechanism is chemical in nature, possibly resulting in the trapping of boron atoms in the oxide. Since the removal of nitrogen would involve the creation of a defect within the oxide, and the creation of such a defect would be detrimental to device performance, we predict that nitrogen will be most effective in suppressing boron indiffusion if it is concentrated near the polycrystalline silicon/oxynitride interface.

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