

# Effect of near-interfacial nitrogen on the oxidation behavior of ultrathin silicon oxynitrides

H. C. Lu, E. P. Gusev, T. Gustafsson, and E. Garfunkel<sup>a)</sup>

*Departments of Physics and Chemistry, and Laboratory for Surface Modification, Rutgers University, Piscataway, New Jersey 08855*

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Medium energy ion scattering has been used to study the role of nitrogen in the thermal oxidation kinetics of ultrathin silicon oxynitrides. Oxynitride films with different amounts of nitrogen near the  $\text{SiO}_x\text{N}_y/\text{Si}$  interface and pure (control)  $\text{SiO}_2/\text{Si}$  films were reoxidized in dry  $^{18}\text{O}_2$  under equivalent conditions. The spatial distribution of  $^{18}\text{O}$  incorporated into the films was analyzed by high-resolution depth profiling methods. Analogous to the pure  $\text{SiO}_2$  case, we observed two distinct regions where oxygen incorporation into the oxynitride films occurs: at/near the interface and near the outer oxide surface. The (near) interface oxide growth reaction is found to be significantly retarded by the presence of near-interfacial nitrogen (with a higher degree of the retardation for higher concentrations of nitrogen). The presence of nitrogen near the interface does not affect the surface exchange reaction. © 1997 American Institute of Physics. [S0021-8979(97)05409-1]

## INTRODUCTION

There is a growing interest in ultrathin (<5 nm) silicon oxynitride films ( $\text{SiO}_x\text{N}_y$ ) for applications as gate dielectrics in next-generation ultra-large-scale integration (ULSI) devices.<sup>1–12</sup> Oxynitride films have improved electrical properties, such as reliability, hot-electron immunity, interface traps, and breakdown strength, and a suppression of boron penetration with respect to conventional ( $\text{SiO}_2$ ) oxides. These beneficial effects have been attributed to the presence of a small amount of nitrogen (typically on the order of  $5 \times 10^{14} \text{ cm}^{-2}$ ) at/near the  $\text{SiO}_x\text{N}_y/\text{Si}$  interface.<sup>1–11</sup>

It is known that near-interfacial nitrogen retards the kinetics of further oxidation of silicon (in  $\text{O}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}$ ).<sup>13,14</sup> However, neither the mechanism of this retardation nor, generally speaking, the mechanism of (re)oxidation of thin oxynitrided films is well understood. Experiments with isotopic substitution of reactive gases [labeled, for example, by  $^{18}\text{O}$  (Refs. 15–17) or  $^{15}\text{N}$  (Ref. 18) atoms] have proven to be powerful in tracing the oxidation reaction and further understanding these mechanisms. Isotopic ( $^{18}\text{O}_2$ ) oxidation of ‘‘pure’’ ( $\text{Si}^{16}\text{O}_2$ ) oxides and subsequent analysis of the profiles of the two isotopes in the film by ion scattering<sup>17,19–21</sup> or nuclear reaction<sup>15,22,23</sup> techniques demonstrated that the traditional model of silicon oxidation, the Deal–Grove model,<sup>24</sup> was insufficient in the limit of ultrathin films. It was shown that, in addition to a classical Deal–Grove-like reaction between diffusing oxygen with the silicon substrate (which occurs at/near the  $\text{SiO}_2/\text{Si}$  interface), there is an additional reaction at the outer oxide surface.<sup>15–17</sup> Unlike the growth reaction at/near the interface, the surface reaction appears to involve mostly an exchange of lattice ( $\text{SiO}_2$ ) oxygen with gaseous  $\text{O}_2$ .

Quite recently, nuclear reaction analysis was used to investigate furnace  $^{18}\text{O}_2$  reoxidation of oxynitrided films.<sup>23</sup> In that work, an initial (8.2 nm) film was grown by rapid thermal oxynitridation of  $\text{Si}(100)$  in  $\text{N}_2\text{O}$ , which resulted in a

small amount of N (less than 2 at. %) distributed within about 5 nm of the interface. The final thickness of the films after reoxidation ranged from 16 to 32 nm. The results of the  $^{18}\text{O}_2$  reoxidation of the oxynitrided film were compared with a 15 nm control oxide grown in oxygen,  $^{16}\text{O}_2/^{18}\text{O}_2$ . (It is important to note here that the control film was grown at a lower temperature and for a much shorter time than the reoxidized oxynitrided films.) It was found<sup>23</sup> that, similar to the oxidation mechanism of the pure ( $\text{SiO}_2$ ) oxide, there are two distinct regions of oxygen reaction with the oxynitride film, viz., the interface and surface reactions. It was concluded,<sup>23</sup> however, that the ratio for the surface reaction is much larger in the presence of nitrogen than for the reoxidation of pure  $\text{SiO}_2$ .

In our work, we have used high-resolution medium energy ion scattering (MEIS)<sup>25</sup> to address the reoxidation behavior of oxynitrided films. This study differs in several ways from the recent nuclear reaction experiment discussed above,<sup>23</sup> specifically: (i) our MEIS apparatus has a higher depth resolution than the nuclear resonant reaction techniques, (ii) the oxidation was studied in the ultrathin (<6 nm) limit, and (iii) both pure  $\text{SiO}_2$  ‘‘control’’ films and reoxidized oxynitrides were grown under exactly the same conditions. In agreement with Ganem *et al.*,<sup>23</sup> we observe two (near-surface and near-interface) regions where  $^{18}\text{O}$  incorporation into oxynitrided films occurs. However, we do not see an effect of the near-interfacial nitrogen on the surface exchange reaction—both the oxynitrided film and the control oxide show similar amounts of  $^{18}\text{O}$  incorporated near the surface if the reoxidation in  $^{18}\text{O}_2$  is performed under the same conditions. In our studies of how the amount of nitrogen near the interface affects the oxidation behavior, we observe that the (near) interfacial reaction becomes significantly retarded with increasing nitrogen content, whereas there is no such effect on the surface reaction.

To study the oxidation behavior of oxynitrided films, we use MEIS with isotopic labeling methods.<sup>17,19–21</sup> The proton beam (97.7 keV) was incident normal to the surface as a probe in these experiments. A high-resolution electrostatic

<sup>a)</sup>Electronic mail: silicon@physics.rutgers.edu

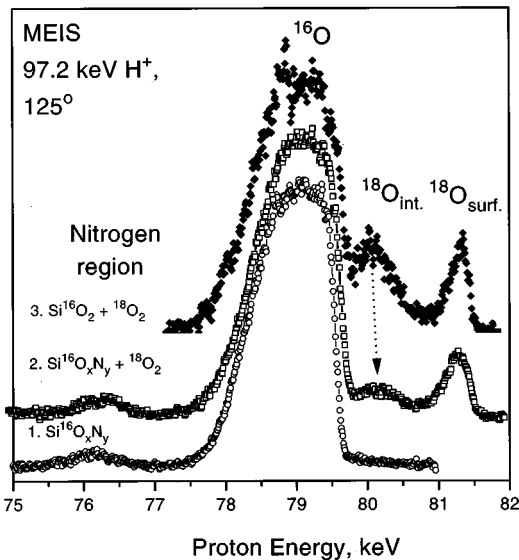


FIG. 1. MEIS spectra in the oxygen and nitrogen regions before (1) and after (2 and 3) re-oxidation in  $^{18}\text{O}_2$  at 920 °C, 7 Torr for 1 h. The original 4.5 nm oxynitrided film (spectrum 1) with  $\sim 7 \times 10^{14} \text{ cm}^{-2}$  of nitrogen localized within  $\sim 1 \text{ nm}$  of the interface was grown by ECR plasma deposition. Spectrum 2 corresponds to the oxynitrided film re-oxidized in  $^{18}\text{O}_2$ . For comparison, spectrum 3 represents a thermally grown  $\text{SiO}_2$  film ( $\sim 4.5 \text{ nm}$ ) re-oxidized in  $^{18}\text{O}_2$ . The spectra are taken in a channeling-blocking geometry with a scattering angle of 125°.

analyzer was used to detect protons backscattered at angles of 115°–135° from Si,  $^{18}\text{O}$ ,  $^{16}\text{O}$ , and N atoms in the films. Further details of the MEIS isotopic oxidation method and high-resolution depth profiling of nitrogen in oxynitrided films can be found elsewhere.<sup>12,19–21</sup> The initial oxynitrided films were prepared by both electron cyclotron resonance (ECR) remote plasma deposition<sup>10</sup> and by thermal (furnace) oxidation<sup>12,26</sup> (in  $\text{N}_2\text{O}$  and  $\text{O}_2/\text{NO}$ ). The thickness of these films was 4.5 and 5.5 nm, respectively. A control  $\text{SiO}_2$  film of similar thickness was grown by rapid thermal oxidation (RTO) (1000 °C). The films were subsequently reoxidized in a quartz furnace in  $^{18}\text{O}_2$  (isotopic enrichment of 98%) for 1 h at 7 Torr and different temperatures in the range of 780–1050 °C. Both the oxynitrided samples and the control samples were reoxidized under similar conditions. Since interfacial nitrogen inhibits oxide growth, the oxynitrided films grew much slower upon reoxidation compared to the control  $\text{SiO}_2$  samples.

## RESULTS AND DISCUSSION

Figure 1 shows MEIS spectra for an oxynitrided film before (spectrum 1) and after (spectrum 2) reoxidation in  $^{18}\text{O}_2$ . Spectrum (3) of the reoxidized control  $\text{SiO}_2$  film is also shown for comparison. The spectrum corresponding to the initial oxynitride film exhibits two peaks, nitrogen and oxygen, (the silicon peak is not shown). The area under the peaks is a measure of the total amount of the nitrogen and oxygen in the film, respectively. One can see that the nitrogen concentration in the film ( $\sim 7 \times 10^{14} \text{ at./cm}^2$ ) is much smaller than that of oxygen. The shape and position of the nitrogen peak is determined by the distribution and location of nitrogen in the film.<sup>12</sup> The width and the position of the

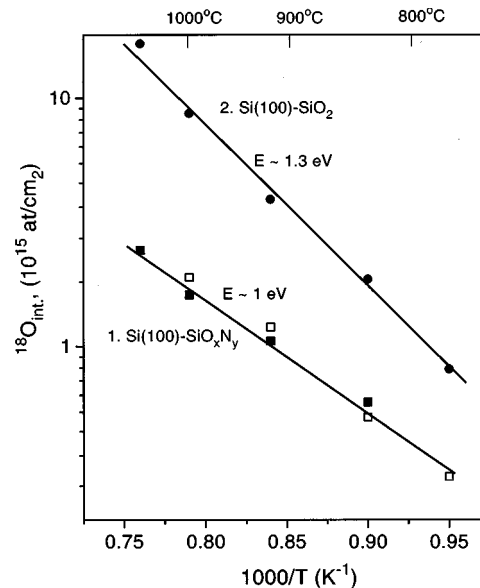


FIG. 2. Semilogarithmic dependence of the amount of  $^{18}\text{O}$  atoms incorporated near the interface after reoxidation ( $^{18}\text{O}_2$ , 7 Torr, 1 h) of the  $\text{SiO}_x\text{N}_y$  (1) and  $\text{SiO}_2$  (2) films on the inverse temperature.

nitrogen peak for the oxynitrided film corresponds to an approximately 1-nm-wide nitrogen distribution adjacent to the  $\text{SiO}_x\text{N}_y/\text{Si}$  interface.

Reoxidation in  $^{18}\text{O}_2$  of both the oxynitride  $\text{SiO}_x\text{N}_y$  film and the control  $\text{SiO}_2$  film results in the appearance of two additional peaks (Fig. 1), originating from protons backscattered off  $^{18}\text{O}$  atoms near the outer oxide surface and near the interface. Oxygen incorporation into these two regions, also observed previously for pure  $\text{SiO}_2$  oxides<sup>15,19–22,27</sup> and oxynitrides,<sup>23</sup> is inconsistent with the traditional Deal–Grove model<sup>24</sup> of silicon oxidation. The intensity of the near-interfacial  $^{18}\text{O}$  peak is much smaller for the oxynitrided film than for the control sample, indicating that the presence of nitrogen significantly retards the growth reaction near the interface. On the other hand, the surface  $^{18}\text{O}$  peak is similar for the two samples implying that the nitrogen at the interface has little effect (if any) on the surface exchange reaction. This observation is not consistent with the recent nuclear reaction study<sup>23</sup> in which it was reported that oxynitrided films exhibit relatively more significant surface exchange. We believe that the reason for this discrepancy may be related to different re-oxidation conditions in the  $\text{SiO}_2$  and  $\text{SiO}_x\text{N}_y$  films in the nuclear reaction study; to achieve a similar thickness the oxynitrided film in Ref. 23 was re-oxidized at higher temperature (1090 vs 1050 °C) and for a longer time (20 vs 2.5 min). One should also note that different oxygen pressures used in the two studies may also effect the surface reaction.

Integrating areas under the  $^{18}\text{O}$  peaks yields the total amount of oxygen incorporated into the near-interface and surface regions. In Fig. 2, we plot (in Arrhenius coordinates) the amount of near-interface ( $^{18}\text{O}$ ) oxygen as function of temperature. One can see that the rate of oxide growth near the interface is almost one order of magnitude lower for the oxynitrided film. For both the oxynitrided sample and the

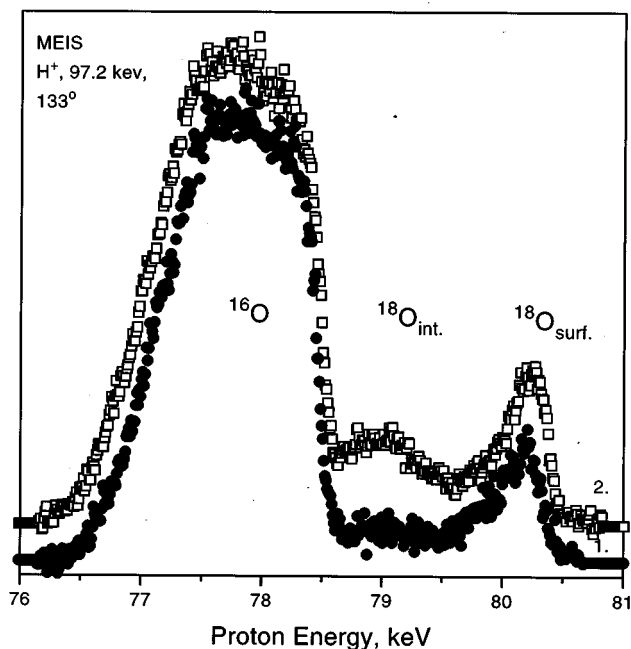


FIG. 3. MEIS spectra in the oxygen region of two ultrathin oxynitrides with different amount of nitrogen after re-oxidation in  $^{18}\text{O}_2$  (920 °C, 7 Torr, 1 h). The oxynitrided film grown in  $\text{O}_2/\text{NO}$  (spectrum 1) has a higher (by almost a factor of 3) concentration of nitrogen near the interface than an  $\text{N}_2\text{O}$  grown oxynitride (spectrum 2). The scattering angle is  $133^\circ$  and the incident ion energy is 97.2 keV.

control sample, the Arrhenius plot shows straight lines with apparent activation energies<sup>28</sup> of about 1.0 and 1.3 eV, respectively. These apparent activation energies are smaller than the value of 2.0 eV for the linear regime of the Deal-Grove model for thermal oxidation of silicon in  $\text{O}_2$ .<sup>24</sup> However, one should keep in mind that, for ultrathin films, the apparent activation energy depends on oxide thickness, and has been shown to decrease with decreasing oxide thickness.<sup>29</sup> For example, it was reported<sup>30</sup> that the initial (<5 nm) RTO oxidation of silicon in dry oxygen has an apparent activation energy of 1.2 eV. For oxynitrided films, our experiments show an even lower apparent activation energy. The elementary processes that contribute to the apparent activation energy remain unclear. Several other recent studies (under different growth conditions) also show that the apparent activation energy of oxidation/oxynitridation of nitrogen-containing films is lower than in the case of pure oxide growth; a 1.5 eV value was obtained for silicon oxynitridation in  $\text{N}_2\text{O}$ <sup>31, 31</sup> about 1 eV for rapid thermal oxynitridation of Si(100) in  $\text{N}_2\text{O}$ <sup>14</sup> (in the temperature range of 850–1000 °C), and 0.7 eV for  $\text{O}_2$  re-oxidation of  $\text{N}_2\text{O}$  grown films.<sup>32</sup>

We have also studied how the concentration of nitrogen near the interface affects the oxidation behavior. For this, two 5.5 nm films with different amounts of incorporated nitrogen were grown by thermal oxidation in  $\text{O}_2/\text{NO}$  and  $\text{N}_2\text{O}$ , respectively. Oxynitridation in  $\text{NO}$  is known<sup>8,12,33</sup> to result in a higher-concentration of nitrogen in a film when compared to  $\text{N}_2\text{O}$  oxynitridation,  $1.1 \times 10^{15}$  at./cm<sup>2</sup> versus less than  $4 \times 10^{14}$  at./cm<sup>2</sup> in our case. Both films were subsequently re-oxidized in  $^{18}\text{O}_2$  under similar conditions. The

spectra shown in Fig. 3 demonstrate a drastic effect of nitrogen on the growth reaction near the interface. At the same time, the amount of  $^{18}\text{O}$  incorporated in the outer surface is very similar for both samples, indicating again that near-interfacial nitrogen has very little effect on the surface exchange reaction.

The effects of nitrogen on the oxidation rate are complex. Two possibilities are that the nitrogen-containing region may: (i) form a diffusion barrier which makes oxygen delivery to the interface more difficult and/or (ii) modify the reaction mechanism for oxide growth near the interface. The first hypothesis is supported by the very low oxygen diffusivity in silicon nitride and oxynitride.<sup>34</sup> The second could result, for example, from nitrogen bonding with “reaction sites” near the interface<sup>35,36</sup> or suppression of Si suboxides (e.g., Si interstitial injection) in the near-interfacial region of the dielectric film.<sup>37</sup> Our preliminary experiments on oxidation of an oxynitride film containing nitrogen near the outer surface also show significant retardation of the interfacial growth reaction, favoring the “diffusion hypothesis.” The mechanism of the surface exchange reaction also remains poorly understood. One model of the surface exchange reaction argues that it results from molecular oxygen interaction with near-surface oxide defects. The absence of a (near-interfacial) nitrogen effect on the surface exchange reaction would thus imply that it is these (near) surface defects or/and high temperature gas phase chemistry rather than the silicon substrate/interface defects that cause the exchange reaction.

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