

# Bonding and band offset in N<sub>2</sub>O-grown oxynitride

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Using high-resolution angle-resolved x-ray photoelectron spectroscopy (ARXPS) measurements, the chemical bonding, and valence-band offset of ultrathin (16 and 24 Å) N<sub>2</sub>O-grown oxide were studied. We confirmed that the composition of N<sub>2</sub>O-grown oxide is mainly silicon oxide with both the concentration and band offset values measured using ARXPS. The surface density of nitrogen is about  $(3 \pm 1) \times 10^{14} \text{ cm}^{-2}$  near the Si/dielectric interface. The valence- and conduction-band offsets for N<sub>2</sub>O-grown oxide are the same as those for the Si/SiO<sub>2</sub> interface because the nitrogen content is too low to have any pronounced effects. In addition, we found that most of the nitrogen atoms at the interface appeared in the form of Si–N bonding instead of N–O bonding. © 2003 American Vacuum Society. [DOI: 10.1116/1.1540989]

## I. INTRODUCTION

It was found that nitrated oxide (oxynitride or SiO<sub>x</sub>N<sub>y</sub>) as the gate dielectric in metal-oxide-semiconductor field-effect transistors (MOSFETs) significantly improves the reliability and device lifetime. This result occurs because oxynitride can suppress the diffusion of impurities, decrease charge trapping in the dielectric, reduce the stress-induced leakage current and interface-state generation, and increase the hardness against radiation.<sup>1–6</sup> There are several methods for nitridation. The as-grown oxide films can be annealed in N<sub>2</sub>O, NO, or NH<sub>3</sub> in a conventional furnace.<sup>7</sup> The self-limited growth of the dielectric in N<sub>2</sub>O results in a low growth rate and this process permits a better control of film thickness.

A bulk amorphous oxynitride SiO<sub>x</sub>N<sub>y</sub> can be prepared by chemical vapor deposition (CVD). Unlike nitrated oxides, bulk oxynitride<sup>8,9</sup> has uniform chemical composition and consists of five types of randomly distributed tetrahedrons of SiO<sub>v</sub>N<sub>4–v</sub>, where  $v = 1, 2, 3,$  and  $4$ . The chemical bonding in N<sub>2</sub>O oxynitride has been studied extensively.<sup>5,7,10,11</sup> However, the bonding or short-range order at the different depths is still unclear. The valence- and conduction-band offsets, or the hole and electron barriers at Si/dielectric interface, are important fundamental parameters. They govern the probability of electron and hole injection, and hence control the lifetime and degradation of MOS devices. It was shown that the valence- and conduction-band offsets at the Si/oxynitride interface depend on the oxynitride chemical composition.<sup>12,13</sup> However, in N<sub>2</sub>O oxynitride, the band offsets have yet to be investigated but it is suggested that the gate oxide film should be reduced to 15–30 Å for future generation of MOS devices; the thickness of the N<sub>2</sub>O oxynitride being prepared

and investigated (in the range of 50–100 Å) is much thicker than the requirement for future MOS devices.<sup>1–7</sup> This article studies the bonding in N<sub>2</sub>O-grown ultrathin oxynitride, and determines the valence- and conduction-band offsets at the Si/dielectric interface.

## II. EXPERIMENT

The starting material is *p*-type silicon with  $\langle 100 \rangle$  orientation and resistivity of about 10 Ω cm. Oxynitride was grown in a conventional furnace in N<sub>2</sub>O ambient at a temperature of 700 °C. Different thicknesses were achieved by varying the N<sub>2</sub>O pressure in the range of 10–450 Torr. Finally, an aluminum contact with area of  $5 \times 10^{-4} \text{ cm}^2$  was defined using photolithography. To measure the physical properties, x-ray photoelectron spectroscopy (XPS) studies were performed with a Kratos AXIS-HS system and a monochromatic Al *Kα* source. High-resolution angle-resolved XPS (ARXPS) studies were carried out on a Phi Quantum 2000 instrument, and the excitation energy was 1486.6 eV.

## III. RESULTS AND DISCUSSION

As measured with the XPS, the total nitrogen surface concentration of the prepared “oxynitride” is about  $(3 \pm 1) \times 10^{14} \text{ cm}^{-2}$ . Here we assumed that the nitrogen is located at the Si/SiO<sub>2</sub> interface and the mean free path of Si 2*p* electrons in SiO<sub>2</sub> is 2.4 nm. This amount is close to the surface density of a half monolayer of solid and is close to the values of other reports.<sup>7,14,15</sup> However, this value is lower by more than a factor of 2 than that reported by Gusev *et al.*<sup>7</sup> This discrepancy is still acceptable. Since the film is so thin and the concentration is so low, any variations in the sample preparation conditions, measurement accuracy as well as the calibration methods will lead to a significant discrepancy.

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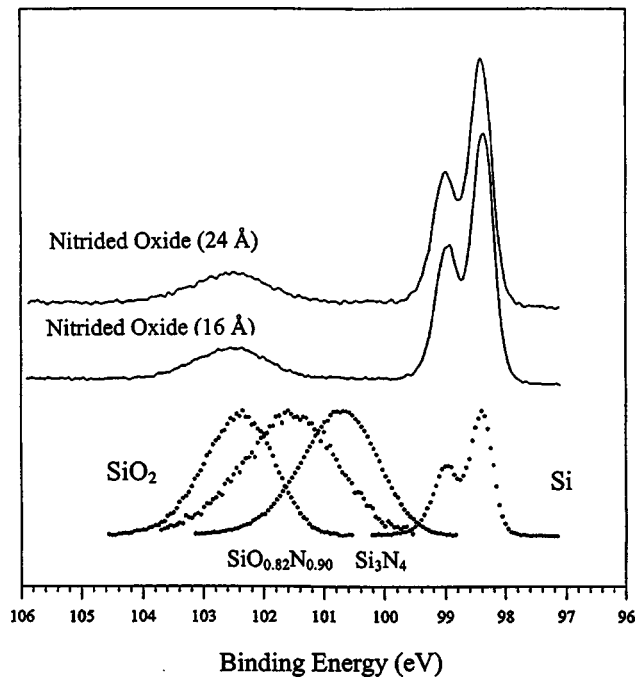


FIG. 1. XPS of Si 2p core level in  $N_2O$ -grown oxide,  $Si_3N_4$ , LPCVD bulk oxynitride ( $SiO_{0.82}N_{0.90}$ ), and thermal  $SiO_2$ .

Since we used rather low oxidation temperature (700 °C) for preparing the ultrathin (1.6 nm) film, the surface concentrations of these samples are expected to be lower than the other studies. In addition, it is found that with 200-eV-Ar beam sputtering the nitrogen distribution is very close (about 5–8 Å) to the Si/dielectric interface. This observation agrees with other studies.<sup>14,16</sup> To understand the chemical bonding, we compared the Si 2p, O 1s, and N 1s spectra of  $N_2O$  oxynitride with the XPS of thermal  $SiO_2$ , low-pressure chemical vapor deposited (LPCVD)  $Si_3N_4$ , and bulk LPCVD oxynitride.

Figure 1 shows the Si 2p spectra of  $N_2O$  oxynitride films with thickness of 24 and 16 Å. Si 2p spectra for  $Si_3N_4$ , LPCVD bulk oxynitride ( $SiO_{0.82}N_{0.90}$ ) and thermal  $SiO_2$  are also depicted in the figure for comparison. It is noted that the Si 2p XPS spectra of  $N_2O$  oxynitride are similar to that of thermal oxide. The Si 2p lines of these samples have the same chemical shift and width. In addition, the O 1s line of  $N_2O$  oxynitride is also similar to the thermal oxide ones. The chemical shifts were studied of O 1s and N 1s in various bulk oxynitride ranging from  $SiO_2$  to  $Si_3N_4$ .<sup>8,9</sup> Compared to these results, it is found that the  $N_2O$  oxynitride used in this investigation is, in fact, a silicon oxide film.

As shown in Fig. 2,  $N_2O$  oxynitride has a different position of N 1s line to that of bulk oxynitride ( $SiO_{0.82}N_{0.90}$ ). Instead, the N 1s line of  $N_2O$  oxynitride has the same energy as that found in silicon nitride, where each nitrogen atom is threefold coordinated by silicon atoms. Hence, the nitrogen atoms in the  $N_2O$  oxynitride are similar to those in the  $Si_3N_4$  structure, i.e., each nitrogen atom is coordinated by three silicon atoms or  $Si_3N$ .<sup>9,17</sup> We did not observe in our  $N_2O$  oxynitride the NO bond, which was proposed in other ex-

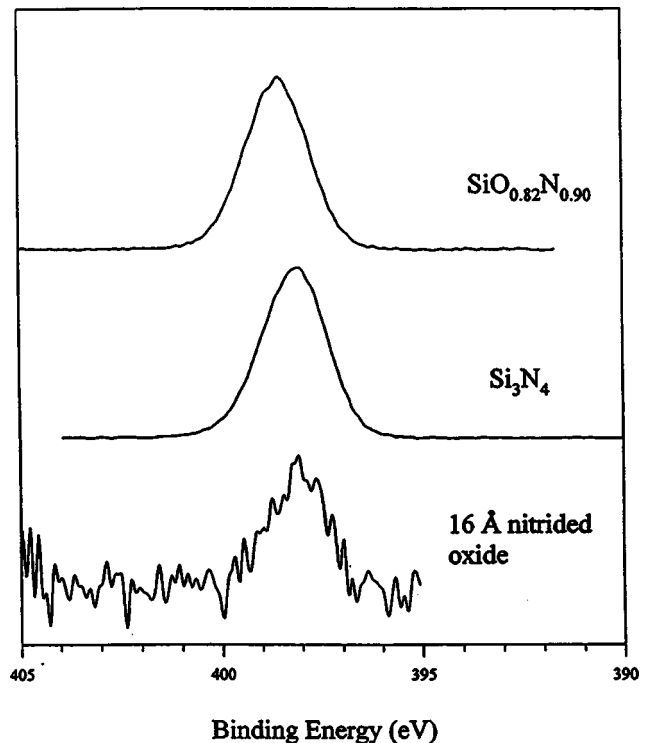


FIG. 2. XPS of N 1s core level of various dielectric films: (a)  $N_2O$ -grown oxide; (b)  $Si_3N_4$ ; and (c) LPCVD bulk oxynitride ( $SiO_{0.82}N_{0.90}$ ).

periments as one of the major constituents of  $N_2O$  oxynitride.<sup>18–20</sup> The existence of NO bonds seems to be process dependent. Bhat *et al.*<sup>18</sup> conducted a comparative study on the chemical structure of  $N_2O$  oxides and reoxidized  $NH_3$ -nitrided oxides. No NO bonds can be found in the reoxidized  $NH_3$ -nitrided oxides. However, in  $N_2O$  oxide, the NO peak is quite significant. Cerofolini *et al.*<sup>20</sup> also conducted a systematic study on the chemical structure of the  $N_2O$  oxides. They found that the existence of NO bonds is governed by the oxidation duration. By oxidation at 850 °C, pronounced NO peak is found for sample oxidized for 10 s; the NO peak disappeared after 1000 s oxidation, however. According to Colquhoun *et al.*<sup>21</sup> the stable oxynitride film should have an atomic structure similar to that of silicon dioxide; that is some of the four oxygen atoms bound to a silicon atom are replaced by nitrogen atoms. Hence, the NO-bond containing structure could not be a stable configuration in the oxide or oxynitride film. Yet the observation of NO bonds at the early stage of nitridation can be attributed to the passivation of silicon dangling bonds with NO radicals. The NO bonds will be transformed to  $Si_3N$  structure after prolonged nitridation. This conjecture explains the experimental results by Bhat *et al.*<sup>18</sup> and Cerofolini *et al.*<sup>20</sup> Further experiments are needed to confirm this conjecture.

To study the electronic structure and determine the valence-band offset between silicon and  $N_2O$  oxynitride, we measured the valence band with ARXPS. It is well known that the Si valence band is formed with Si 3s, 3p electronic states, and the valence band of silicon oxide is formed with O 2p, Si 3s, 3p, 3d bonding states and O 2p $_{\pi}$ , nonbonding

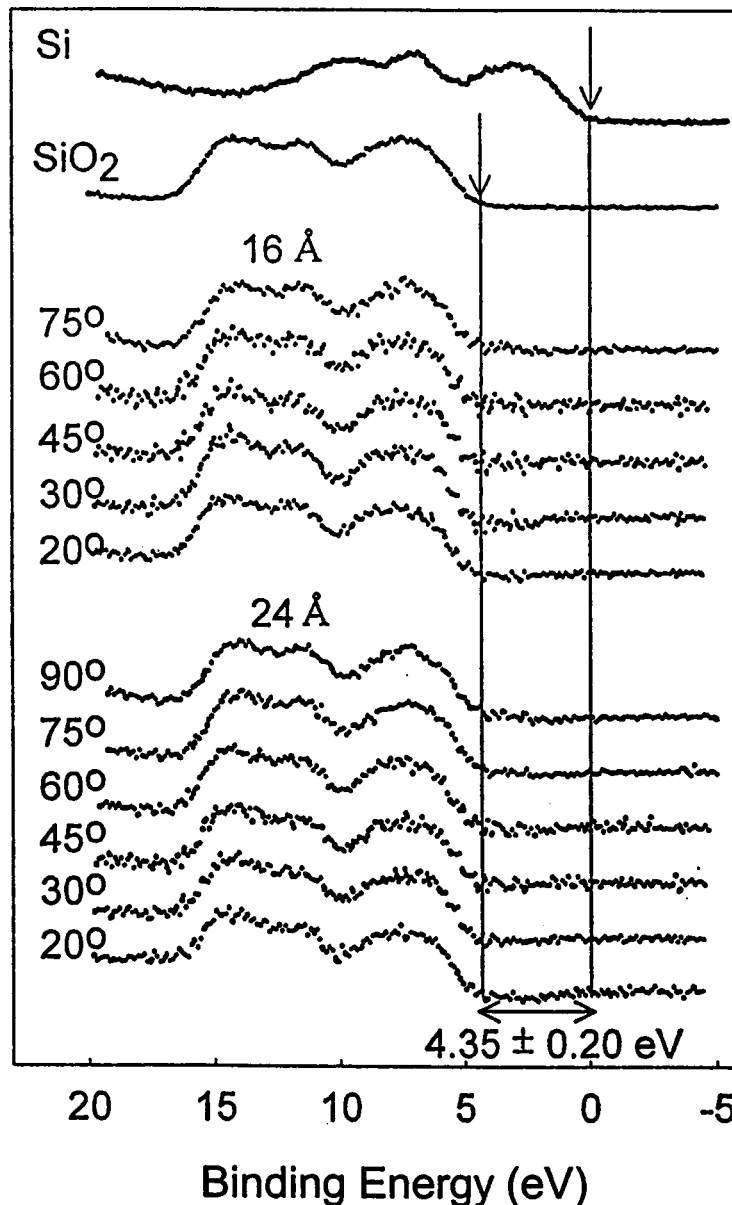


Fig. 3. Angle-resolved XPS of N<sub>2</sub>O-grown oxide after taking off the Si XPS component. XPS for Si and SiO<sub>2</sub> valence bands are also shown for comparison.

states.<sup>22</sup> The SiO<sub>x</sub>N<sub>y</sub> valence band is formed with Si 3*s*, 3*p*, 3*d*, O 2*p*, N 2*p* bonding states and O 2*p*<sub>π</sub>, N 2*p*<sub>π</sub> nonbonding states.<sup>9</sup> Using XPS measurements with an excitation energy of 1486.6 eV, it was found that the dominant contribution to the SiO<sub>x</sub>N<sub>y</sub> valence band is 85% from Si 3*s* and 15% from Si 3*p* states.<sup>23</sup> The contributions of Si 3*d*, O 2*p*, and N 2*p* states to XPS spectra are negligible. In SiO<sub>x</sub>N<sub>y</sub> and SiO<sub>2</sub> films, although the top of the valence band is formed mainly by N 2*p* and O 2*p* states, these states do not contribute to the XPS valence band because of their small ionization cross section. Hence, if the top of the valence band of SiO<sub>2</sub> is estimated to be  $E_v - 0.5$  eV using the XPS measurement and it is assumed that the major contribution is from the O 2*p* states, then the band offset at the Si/SiO<sub>2</sub> interface may be overestimated by about 0.5 eV.

Figure 3 shows the valence-band ARXPS at the

N<sub>2</sub>O-grown oxynitride/Si interface with different thicknesses of oxynitride. The XPS results of a thermal SiO<sub>2</sub> and Si are also shown for comparison. The ARXPS spectra are a superposition of signals from silicon and the dielectric. As shown in Fig. 3, the small-angle XPS spectra of N<sub>2</sub>O-nitrided oxide is different from the valence-band XPS of the bulk oxynitride (SiO<sub>0.82</sub>N<sub>0.90</sub>), but is similar to XPS spectra of bulk SiO<sub>2</sub>. This implies that the valence-band electronic structure of N<sub>2</sub>O-nitrided oxide should be similar to SiO<sub>2</sub>, rather than to a bulk oxynitride. This result once again suggests that the N<sub>2</sub>O-nitrided oxide is, in fact, an oxide rather than an oxynitride. By subtracting the oxide film spectra with Si spectra, the valence-band offset between Si and N<sub>2</sub>O-nitrided oxide is found to be  $4.5 \pm 0.1$  eV. This value is in good agreement with the data at the Si/SiO<sub>2</sub> interface.<sup>24</sup>

To determine the conduction-band offset, we measured

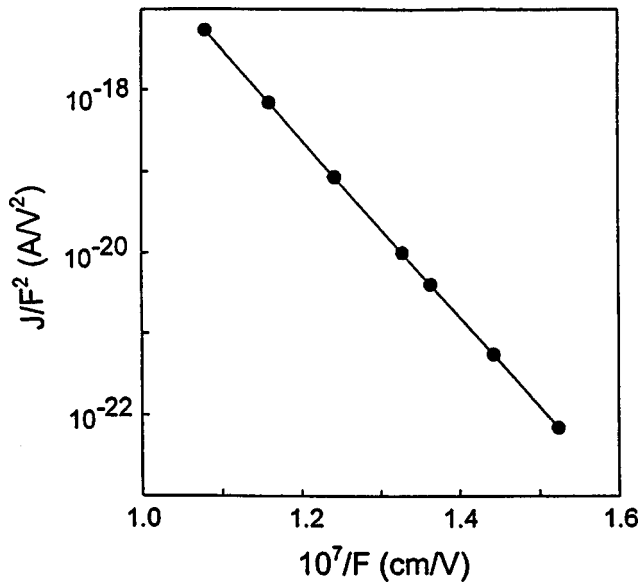
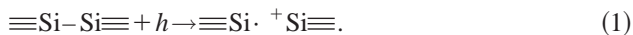


FIG. 4. Current–voltage characteristic of Si/N<sub>2</sub>O-grown oxide/Al structures. Negative potential is applied to Si side.

the current conduction of a MOS structure with a gate dielectric grown by N<sub>2</sub>O oxidation. By applying a negative potential to the silicon side, charge transport from the silicon substrate into the dielectric via Fowler–Nordheim electron injection occurs.<sup>25</sup> The current–voltage ( $I$ – $V$ ) characteristic is depicted in Fig. 4. Assuming that the effective mass of electron ( $m^*$ ) in the conduction band is  $0.5 m_0$ , the electron barrier at the Si/dielectric interface can be extracted from the  $I$ – $V$  curve and is  $2.9 \pm 0.1$  eV. The extracted value is lower than that (3.15 eV) at the Si/SiO<sub>2</sub> interface<sup>26</sup> but is the same as the obtained from the oxynitride grown by rapid thermal N<sub>2</sub>O nitridation.<sup>4</sup> Weinberg explained this small barrier value by the electron quantization effect in silicon.<sup>25</sup>

The nitrogen incorporation at the Si/oxynitride interface results in the removal of Si–Si bonds.<sup>17,27</sup> A neutral Si–Si bond is a hole trap in SiO<sub>2</sub>, and the hole capture takes place via the following reaction:



The positively charged  $\equiv\text{Si}^+\text{Si}\equiv$  defect (or  $E'$  center in SiO<sub>2</sub>) is a well-known trap responsible for the positive charge accumulation during irradiation or hot carriers injection.<sup>28,29</sup> Using XPS measurement, Lu *et al.*<sup>19</sup> revealed that the density of Si–Si bonds at the interface is in the range of  $(2.2-12) \times 10^{15} \text{ cm}^{-2}$ . Green *et al.*<sup>14</sup> and Tobin *et al.*<sup>15</sup> also found that the density of nitrogen at the interface of Si/oxynitride (by N<sub>2</sub>O oxidation) is in the range  $(2-14) \times 10^{14} \text{ cm}^{-2}$ . Based on the Mott rule,<sup>17</sup> the nitrogen atoms can react with Si–Si bonds via the following reaction:



This reaction results in the removal of Si–Si bonds and reduces hole capturing. The resulting film will have greater radiation hardness due to less hole capturing.

It is well known that the dominant source of surface states at the Si/SiO<sub>2</sub> interface is due to  $P_b$  centers.<sup>30-32</sup> A  $P_b$  center is a threefold-coordinated silicon atom with an unpaired electron (i.e.,  $\equiv\text{Si}_3\text{Si}$ ) and is an electron and hole amphoteric surface center at the Si/SiO<sub>2</sub> interface. Without hydrogen passivation, Gosset *et al.*<sup>33</sup> found that the oxide nitridation could result in the decrease of  $P_b$  center density from  $2 \times 10^{12} \text{ cm}^{-2}$  to a value below  $10^{11} \text{ cm}^{-2}$ . This is our desired interface property of an oxynitride film.

According to the Mott rule, the suppression of  $P_b$  centers during nitridation can also be explained with the incorporation of nitrogen atoms on the silicon surface according to the following reaction:



With this reaction, nitrogen atom incorporation during nitridation accompanies the removal of Si–Si bonds and the silicon dangling bonds ( $\equiv\text{Si}$ ). The resulting species ( $\equiv\text{Si}_3\text{N}$ ) are chemically and electrically stable.

#### IV. CONCLUSIONS

In summary, our XPS study reveals that the oxynitride prepared by N<sub>2</sub>O oxidation is, in fact, essentially a thermal oxide. The nitrogen content is very low, and the nitrogen atoms create the Si<sub>3</sub>N species at the Si/dielectric interface. The valence- and conduction-band offsets of N<sub>2</sub>O oxynitride are the same as that at the Si/SiO<sub>2</sub> interface. Removal of Si–Si bonds and  $P_b$  centers during nitridation occurs and is explained by the creation of Si–N bonds.

#### ACKNOWLEDGMENT

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