

Characterization and modeling of the nitrogen passivation of interface traps in SiO₂/4H–SiC

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The relationship between nitrogen content and interface trap density (D_{it}) in SiO₂/4H–SiC near the conduction band has been quantitatively determined. Nitridation using NO significantly reduces D_{it} near the conduction band, but the effect saturates after $\approx 2.5 \times 10^{14} \text{ cm}^{-2}$ of nitrogen. These results are consistent with a model of the interface in which defects such as carbon clusters or silicon suboxide states produce traps with energies corresponding to the sizes of the defects. Nitrogen passivation results in the dissolution of the defects, which then lowers the energies of the traps in the band gap. © 2003 American Institute of Physics. [DOI: 10.1063/1.1542935]

I. INTRODUCTION

Silicon carbide is a wide band gap semiconductor that has attracted great interest for power applications because it thermally oxidizes to form SiO₂, which offers the possibility of manufacturing metal–oxide–semiconductor field-effect transistors (MOSFET's). Among the commercially available SiC polytypes, 4H–SiC has the highest and most isotropic electron mobility; however, MOSFET's fabricated from 4H–SiC may exhibit channel mobilities ~ 100 times lower than the bulk value and ~ 10 times lower than other polytypes like 6H and 15R–SiC.^{1,2} Schörner *et al.*¹ speculated that the poor mobility is caused by a large density of interface traps (D_{it}) beginning at ≈ 3 eV from the valence band in all SiC polytypes.¹ In 6H–SiC ($E_G = 3.02$ eV), most of these traps are located in the conduction band, which minimizes their effects; however, these traps are within the band gap of 4H–SiC ($E_G = 3.26$ eV) and can exchange charge with the SiC, degrading the mobility. Experimental data confirm that D_{it} increases rapidly to values of $\sim 10^{13} \text{ cm}^{-2} \text{ eV}^{-1}$ near the conduction band of 4H–SiC.^{3,4}

Two likely sources of these interface defects are carbon clusters and silicon suboxide bonds. The oxidation of SiC forms SiO₂ and CO, which diffuse out of the oxide bulk and remove carbon; however, residual carbon remains at the interface after oxidation with a density as high as $\sim 10^{15} \text{ cm}^{-2}$.^{5,6} Afanas'ev *et al.*^{7,8} theorized that this carbon forms graphitelike clusters that produce a series of trap levels distributed across the band gap.^{7,8} It is also known that silicon suboxide bonds exist at both the Si/SiO₂ and SiC/SiO₂ interfaces,^{6,9} and the density of these defects is estimated to be $\sim 10^{15} \text{ cm}^{-2}$ in silicon. These suboxide defect states evidently do not lie within the band gap of silicon, as shown by the low D_{it} values achievable in Si/SiO₂, but these states may be within the band gap of SiC.^{10,11}

Excess silicon and carbon could be intrinsic components of the transition layer between SiC and SiO₂, and their complete removal from the interface may not be possible.^{12,13} Instead, the passivation of these defects with additives like nitrogen might be used to change the energy of these states in the band gap and reduce their detrimental effects. Nitridation using NO and NH₃ provides an effective technique for reducing D_{it} in SiO₂/4H–SiC near the conduction band and increasing the channel mobility.^{14–17} Nitridation using NO incorporates nitrogen only at the SiO₂/SiC interface,^{18–20} while NH₃ incorporates nitrogen uniformly throughout the oxide.²¹ The reduction in D_{it} is identical for both techniques, however, which indicates that interfacial nitrogen is the critical factor.

Density-functional calculations suggest that both graphitelike carbon clusters and silicon suboxide bonds place states in the band gap near the conduction band.^{15,22} When passivated with nitrogen, these states are lowered to energies in and near the valence band. Experiments confirm that D_{it} increases near the valence band of 4H–SiC after nitridation.¹⁵ In the case of carbon clusters, the energy of a defect increases toward the conduction band with the size of the cluster. The single-atom defect is the most stable, and passivation may involve the dissolution of large clusters by removing smaller nitridized carbon clusters.¹⁰ In this article, the relationship between interfacial nitrogen content and trap density in SiO₂/4H–SiC is investigated, and a model for the nitrogen passivation of these traps is presented.

II. EXPERIMENTAL DETAILS

To measure the interface trap density near the conduction band of 4H–SiC, metal–oxide–semiconductor capacitors were manufactured using *n*-type, Si-faced 4H–SiC wafers with 10 μm epitaxial layers doped to a concentration of 10^{16} cm^{-3} . Before oxidation, samples were prepared using the Radio Corporation of America (RCA) cleaning technique. The samples were oxidized in a wet ambient at 1100 °C for 4 h to produce an oxide thickness of 35 nm.²³ A

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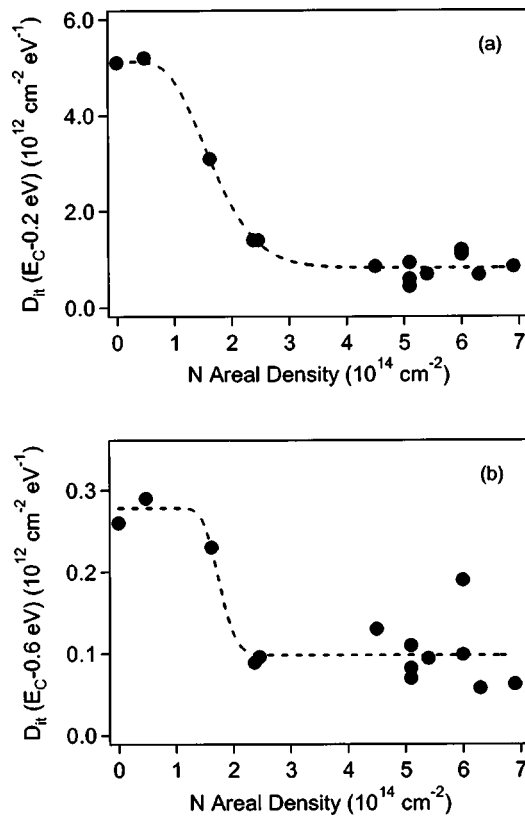


FIG. 1. Interface trap density D_{it} in $\text{SiO}_2/4\text{H-SiC}$ at (a) 0.2 eV and (b) 0.6 eV from the conduction band E_C as a function of nitrogen areal density.

postoxidation anneal in Ar was performed at 1100 °C for 30 min, followed by a reoxidation anneal at 950 °C for 3 h. Nitridation of the oxides was completed by annealing in NO flowing at ~ 0.3 L/min at 1 atm at temperatures from 1050 to 1175 °C for 0.5, 2, and 6 h. Because NO incorporates nitrogen only at the interface, the correlation between nitrogen content and D_{it} is more straightforward. The nitrogen content was determined from previous measurements using nuclear reaction analysis and secondary ion mass spectrometry.²⁰

Molybdenum gate contacts were sputter deposited, and silver paint was applied to the back side for an ohmic contact. The interface trap density was measured with the simultaneous high–low capacitance–voltage technique at energies from 0.2 to 0.6 eV from the conduction band. Measurements were performed at room temperature, and the gate bias was swept from accumulation to inversion.

III. RESULTS AND DISCUSSION

The interface trap densities at 0.2 and 0.6 eV from the conduction band as a function of nitrogen content are shown in Fig. 1. Nitridation reduces D_{it} at all energies from 0.2 to 0.6 eV, but the effect is greatest near the conduction band. The maximum trap reduction is close to one order of magnitude at 0.2 eV, but is only a factor of 3 at 0.6 eV. Note that nitridation has no effect on D_{it} for nitrogen amounts less than $\approx 10^{14} \text{ cm}^{-2}$, indicating that a substantial amount of nitrogen must be incorporated before the onset of detectable trap reduction. This “passivation threshold” increases with the en-

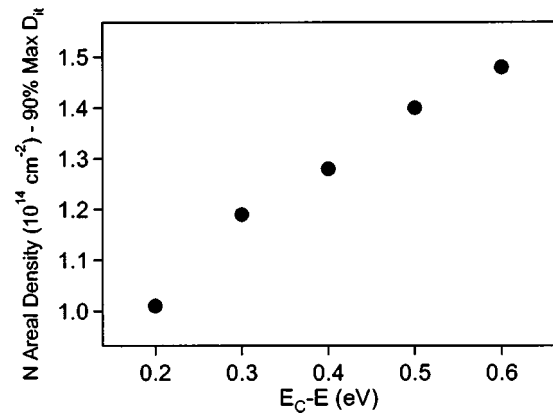


FIG. 2. Nitrogen areal density needed to reduce the interface trap density D_{it} to 90% of its maximum value as a function of energy from the conduction band E_C .

ergy from the conduction band, from $\approx 1 \times 10^{14} \text{ cm}^{-2}$ at 0.2 eV to $\approx 1.5 \times 10^{14} \text{ cm}^{-2}$ at 0.6 eV (Fig. 2).

For nitrogen amounts above this threshold, trap reduction is rapid and saturates at a nitrogen content of $\approx 2.5 \times 10^{14} \text{ cm}^{-2}$. This passivation depends only on the nitrogen content, not the NO anneal time or temperature. For example, nitridation at either 1050 °C for 2 h or 1100 °C for 0.5 h produces a similar nitrogen content, $\approx 2.4 \times 10^{14} \text{ cm}^{-2}$, and trap density at all energies. The amount of nitrogen required for the complete passivation of these traps is $\sim 1/4$ of a monolayer of (0001) 4H-SiC, which is much greater than the total density of traps, $\sim 10^{12} \text{ cm}^{-2}$.

These data and Refs. 1, 7, 10, 16, and 22 suggest a possible model of the nitrogen passivation of interface traps in $\text{SiO}_2/4\text{H-SiC}$ with the following assumptions. Each interface defect is a cluster of atoms that introduces a trap level near the conduction band of 4H-SiC. The energy of this state corresponds directly to the size of the cluster, with the largest cluster at the highest energy. These clusters vary in size and produce a series of associated trap levels in the band gap.

When an atom in a cluster is passivated with a nitrogen atom, it is removed from the cluster. The passivated atom then introduces a trap state in or near the valence band, and the energy of the remaining cluster is shifted lower in the band gap by one trap level. For example, when a three-atom carbon cluster is passivated by a nitrogen atom, it becomes a lower-energy two-atom cluster, $\text{C}_3 + \text{N} \rightarrow \text{C}_2 + \text{CN}$; when a two-atom cluster is passivated, it becomes a lower-energy single-atom defect, $\text{C}_2 + \text{N} \rightarrow \text{C} + \text{CN}$, and so on. During nitridation, therefore, the trap density in an energy level decreases when a cluster in that level is passivated and increases from the “feeding in” process when a cluster in the level above is passivated.

In the simplest representation, cluster passivation results from the random collisions between clusters and nitrogen atoms. The change in the occupancy of a cluster level is, therefore, expected to be proportional to the number of clusters in that level and the change in nitrogen content. From the trap level of the largest cluster containing m atoms to the

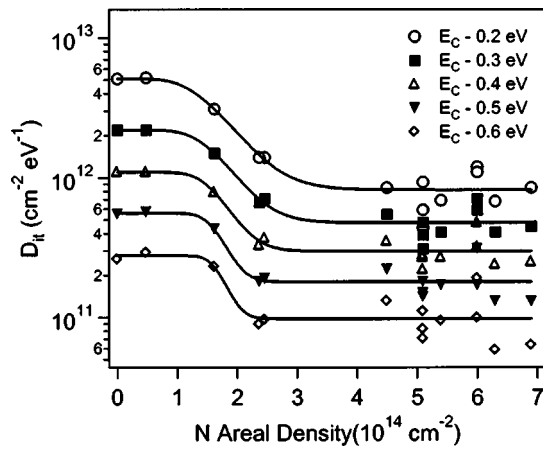


FIG. 3. Interface trap density D_{it} as a function of nitrogen areal density at energies 0.2–0.6 eV from the conduction band E_c fitted using Eq. (3) and the parameters in Table I.

level of a single atom, the changes in the trap density due to nitridation are given by

$$\begin{aligned}
 \Delta T_m &= -R_m T_m \Delta N, \\
 \Delta T_{m-1} &= -R_{m-1} T_{m-1} \Delta N + R_m T_m \Delta N, \\
 &\vdots \\
 \Delta T_i &= -R_i T_i \Delta N + R_{i+1} T_{i+1} \Delta N, \\
 &\vdots \\
 \Delta T_1 &= -R_1 T_1 \Delta N + R_2 T_2 \Delta N,
 \end{aligned}
 \tag{1}$$

where T_i is the trap density in the i th atom level, R_i is the cross section for nitrogen passivation of a cluster at level i , and N is the nitrogen content.

The solution of Eq. (1) is a series of exponential terms that is complex and unwieldy for as few as three levels. A simple approximation can be made, however, by expanding the exponential terms and making two assumptions: (1) the initial trap densities decrease monotonically with energy from the conduction band, and (2) the passivation cross section R_i increases monotonically with energy from the conduction band. As shown in Fig. 3, the first assumption is valid for 0.2–0.6 eV from the conduction band. These assumptions allow the solution for the trap density in any level i to be represented solely in terms of the initial trap density and passivation cross section of level i . The trap density in level i as a function of nitrogen content is then approximated by

$$\begin{aligned}
 T_i(N) &= T_{i0} e^{-R_i N} (1 + R_i N + (R_i N)^2 / 2! + \dots \\
 &\quad + (R_i N)^{m-i} / (m-i)!).
 \end{aligned}
 \tag{2}$$

The trap density in level i is thus the product of the initial trap density T_{i0} , $e^{-R_i N}$, and the series expansion of $e^{R_i N}$ up to order $m-i$. The series represents the contribution to the trap density from each level above i (up to level m) due to the feeding in process that occurs during nitrogen passivation. The $e^{-R_i N}$ term represents the reduction in trap density from nitrogen passivation.

Using Eq. (2), the total interface trap density D_{it} at an energy E as a function of nitrogen content N is given by

$$D_{it}(E; N) = L(E) + T_0(E) e^{-R(E)N} \sum_{j=0}^{n(E)} \frac{(R(E)N)^j}{j!}.
 \tag{3}$$

The parameter L represents noncluster traps that are not passivated by nitrogen and cause the observed D_{it} saturation at high nitrogen amounts. The sum limit n represents the number of cluster levels above the energy E , not the size of the cluster at energy E . The parameters T_0 and R are the initial trap density and passivation cross section, respectively, at energy E .

The interface trap density as a function of nitrogen content was fit with Eq. (3) from 0.2 to 0.6 eV from the conduction band using the following procedure. At each energy, a value of n was chosen, and the parameters L , R , and T_0 were determined using a least-squares fitting algorithm; the value of n was then changed, and the fitting routine applied again. The best set of parameters was determined using the minimum value of χ^2 . Based on the differences in χ^2 , the error in n was $\approx 20\%$; the fitting routine was implemented only to $n=60$ at 0.6 eV, but the differences in χ^2 were small for n values from 50 to 60.

The fits to the data are excellent for all energies (Fig. 3), and the fitting parameters are listed in Table I. The value of n increases monotonically with the energy from the conduction band, which is consistent with the assumed distribution of traps in this model. Clusters of at least 60 atoms are predicted from these calculations, but larger clusters are possible since the data are not analyzed below 0.6 eV from the conduction band. The large number of trap levels obtained with this model suggests that these defect states do not exist as discrete levels, but instead approach a near continuum of energy levels.

The value of R also increases monotonically with energy from the conduction band, which is consistent with the initial assumption in this approximation. The trap densities in the lower-energy levels are, therefore, passivated faster than the

TABLE I. Parameters used in Eq. (3) to fit the data in Fig. 3.

$E_c - E$ (eV)	n	T_0 ($10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$)	R (10^{-14} cm^2)	L ($10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$)
0.2	7	43	4.6	8.2
0.3	11	17	6.7	4.8
0.4	20	8	11	3.0
0.5	40	3.8	23	1.8
0.6	60	1.8	33	0.98

higher-energy levels. This result, coupled with the decreasing values of T_0 , explains the nitrogen passivation behavior as follows.

The traps at lower energies are passivated relatively quickly, but since the trap density is larger at higher energies, traps are feeding in at the same rate as they are being passivated out of a level. The trap density in a level therefore remains nearly constant until the higher-energy levels are completely passivated, and it is only at this point that the trap density decreases. This process causes the nitrogen passivation threshold seen at $\approx 10^{14} \text{ cm}^{-2}$. Lower-energy levels require more nitrogen for complete passivation because of the greater number of high-energy levels, which results in the threshold shift observed from 0.2 to 0.6 eV from the conduction band. Excess nitrogen above the threshold has no effect on the trap density because all traps in that level and higher are completely passivated, leading to the observed saturation at $\approx 2.5 \times 10^{14} \text{ cm}^{-2}$.

This model also provides a simple explanation of the need for $\approx 2.5 \times 10^{14} \text{ cm}^{-2}$ of nitrogen to passivate a trap density of $\sim 10^{12} \text{ cm}^{-2}$. Each defect cluster produces a single-trap level regardless of the size of the cluster, but the dissolution process implies that complete passivation requires one nitrogen atom for each atom in the cluster. The sum of all atoms in all defect clusters available for passivation is evidently $\approx 2.5 \times 10^{14} \text{ cm}^{-2}$, which is consistent with the amount of excess silicon or carbon at the interface.

The dynamics of nitrogen passivation are approximated well using only the three parameters n , T_0 , and R . An exact solution of Eq. (1) is unlikely to yield better results. The subsequent equations would be complicated, especially for a large number of levels, and the number of parameters required would be greater than the number of data points, which makes meaningful data fitting impossible.

IV. CONCLUSIONS

The nitridation of $\text{SiO}_2/4\text{H-SiC}$ in NO significantly reduces the interface trap density near the conduction band; however, the effect saturates at $\approx 2.5 \times 10^{14} \text{ cm}^{-2}$ of nitrogen, leaving a trap density that is still higher than silicon. Trap passivation depends only on the nitrogen content and is independent of the annealing conditions. The data are consistent with a model of the interface in which a near continuum of trap levels near the conduction band is produced by large defect clusters composed of excess interfacial carbon or silicon. Nitrogen passivation of these traps proceeds with the dissolution of the clusters by the removal of nitridized atoms.

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