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Two-fold coordinated nitrogen atom: an electron trap in MOS devices with silicon oxynitride as the gate dielectric

Yu.N. Morokov[a], Yu.N. Novikov[b], V.A. Gritsenko[b], and H. Wong[c]

[a]Institute of Computational Technologies, Novosibirsk, 630090, Russia
[b]Institute of Semiconductor Physics, Novosibirsk, 630090, Russia
[c]Department of Electronic Engineering, Cityu, Tat Chee Avenue, Hong Kong

Having conducted semiempirical quantum-chemical simulation (MINDO/3) of several clusters at different charge states, we identify that the two-fold coordinated nitrogen atom with an un-paired electron (≡Si_2N•) is the most responsible trap center for the observation of large electronic capturing in SiO_xN_y. Our calculations also show that electron localized in this defect will result in spin dissipation. Trap formation and removal mechanisms during nitridation and re-oxidation are also discussed in this work.

1. INTRODUCTION

The properties of gate dielectric determine the reability of metal-oxide-semiconductor (MOS) devices. It was suggested that the conventional silicon dioxide gate dielectric should be replaced by silicon oxynitride (SiO_xN_y) in the future nanoscale MOSFET to minimize the hole and electron trapping on Si-Si defects at the Si/SiO_2 interface. It was demonstrated that the Si-Si defects could be removed effectively by high-temperature annealing of thermal SiO_2 in ammonia. This process can be described as follow [1]:

$$3 \equiv\text{Si-Si}\equiv + 2\,\text{N} \rightarrow 2 \equiv\text{Si}_3\text{N} \qquad (1)$$

The symbols –, = and ≡ in (1) represent one single bond, two single bonds, and three single bonds, respectively. With oxynitride as the gate dielectric, hole trapping was reduced considerably. However, large amount of electron traps are still found in oxynitride and degradation of MOSFET due to the capturing of hot channel electrons is often reported. In present paper we show, using semiempirical quantum-chemical method MINDO/3, that the two-fold coordinated nitrogen atom with unpaired electron ≡Si_2N• is the trap responsible for the capturing of electrons in ammonia-nitrided SiO_xN_y. Here • denotes the one unpaired electron. MINDO/3 had been shown to be a powerful and informative method for simulating electronic structure and bulk defect in solid [2-3].

2. SIMULATION RESULTS

In this work, we used the cluster approximation to study the electronic structure of several different clusters in silicon oxynitride. Atomic relaxation in different charge states of defect was considered in the simulation. To simulate the effect of chemical composition on the capturing properties of the ≡Si_2N• defect in silicon oxynitride, clusters with different numbers of oxygen and nitrogen atoms, i.e. •$NSi_2(N_6)SiH_{12}$, •$NSi_2(N_4O_2)SiH_{10}$, and •$NSi_2(O_6)H_6$, in the second coordination sphere were considered. For simulation of the Si_3N_4 bulk electronic structure we used the $Si_{20}N_{28}H_{36}$ cluster. The atomic structures of these clusters are shown in Fig.1. MINDO/3 parameters used in this work are same as those used in Ref. [3-4] which are α_{SiN} = 1.053011 and β_{SiN} = 0.434749.

Simulation of the neutral ≡Si_2N• defect shows that unpaired electron is localized for all considered clusters in the N $2p_\pi$ nitrogen non-bonding orbital which is oriented normally to the Si_2N plane. This result agrees with the previous theoretical simulation of this defect in silicon nitride [5]. As

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obtained in ref. [6] for the ≡Si_2N• defect in Si_3N_4, the wave function of the unpaired electron consists from 90% of p-type and 10% of s-type atomic functions. Similar result was also obtained from the analysis of ESR signal hyperfine splitting in SiO_xN_y [7]. Our calculations show that the distribution of the unpaired electron in the defect nitrogen atom are 96% and 4% for p-type and s-type wave function, respectively. The difference between experimental and simulation result may be due to the small cluster being used in the simulation.

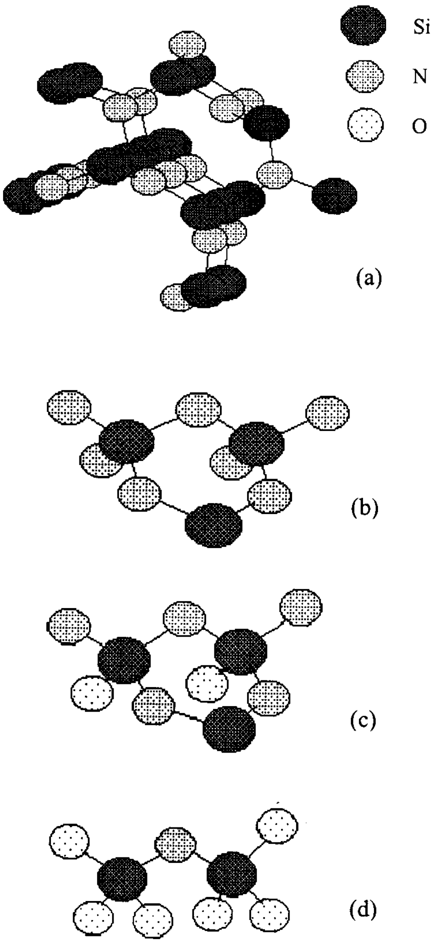

Fig. 1. Clusters used in simulating the defect capturing properties of (a) $Si_{20}N_{28}H_{36}$, (b) •$NSi_2(N_6)SiH_{12}$, (c) •$NSi_2(N_4O_2)SiH_{10}$, and (d) •$NSi_2(O_6)H_6$.

It was found experimentally that cross-section for the capture of electron (σ) in SiO_xN_y is about 10^{-17} cm^2. This value corresponds to an effective capture radius of the trap $R = \sqrt{\sigma / \pi}$ ≈ 0.2 Å. This value reflects the highly localized character of the non-bonding N $2p_\pi$ wave function and supports our simulation results.

We also estimated the energy gain for the electron or hole capturing in the ≡Si_2N• defect by calculation of the differences between the total energies of clusters in different charge states. Figure 2 shows the calculated energy diagram for ≡Si_2N• and ≡SiO• defects in oxynitride. Similar defects in oxide and nitride are also shown for comparison. The obtained values of the energy gain for the capture of electron from the bottom of the conduction band (E_c) is about 1.0 eV. That is the thermal delocalization electron trap energy is about 1.0 eV. However, the capture of hole from the top of the valence band (E_v) is energetically unfavorable. In addition, simulation results also show that the electron trap energy is almost independent on the cluster chemical composition. The energy gain results indicated that the ≡Si_2N• defect in silicon nitride and oxynitride with high concentration of nitrogen cannot capture a hole but an electron. The captured electron is localized in the N $2p_\pi$ non-bonding orbital of the ≡Si_2N• defect (see Fig.3).

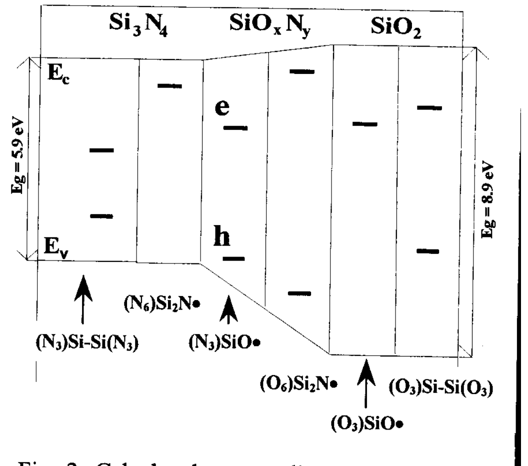

Fig. 2. Calculated energy diagram for the major defects in oxynitride. Similar defects in oxide and nitride are also shown for comparison.

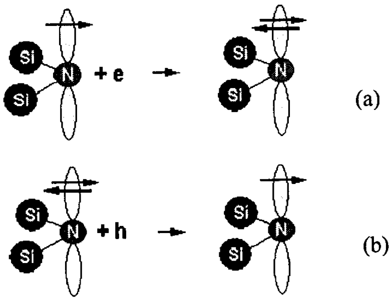

Fig. 3. Model of three-fold coordinated nitrogen atom as an electron trap in silicon nitride and oxynitride (a) capture of electron, and (b) capture of hole.

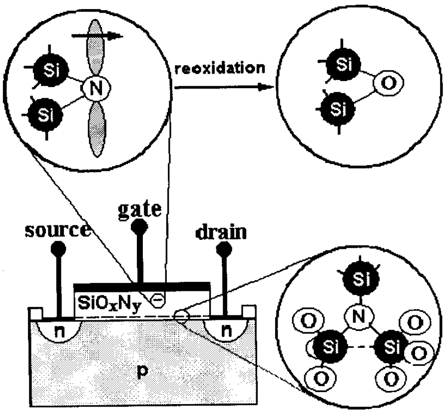

Fig. 4. Illustration of $\equiv Si_2N\bullet$ centers in oxynitride and the removal of electron traps during re-oxidation of oxynitride in MOSFET.

3. DISCUSSION

According to the obtained results, the capture (localization) and following decapture (delocalization) of electron on the $\equiv Si_2N\bullet$ defect in Si_3N_4 and SiO_xN_y are described by the following reactions:

$$
\begin{aligned}
&\equiv Si_2N\bullet + e \rightarrow \equiv Si_2N: \\
&\equiv Si_2N: + h \rightarrow \equiv Si_2N\bullet
\end{aligned}
\qquad (2)
$$

Electron localization results in the transfer of paramagnetic defect $\equiv Si_2N\bullet$ to diamagnetic defect $\equiv Si_2N:$. The corresponding model is picturized in Fig.3. Our simulation predicts the electron paramagnetic signal dissipation at the electron capture by three-coordinated nitrogen atom, which was observed experimentally in nitrided oxide [7].

It has been confirmed that the $\equiv Si_2N\bullet$ is the major defect in SiO_xN_y. The $\equiv Si_2N\bullet$ defect creation in SiO_xN_y could be resulted from the breaking of the Si_2N-H bond according to the following reaction

$$\equiv Si_2NH \rightarrow \equiv Si_2N\bullet + H \qquad (3)$$

Another mechanism for the creation of $\equiv Si_2N\bullet$ defect is the breaking of N-N bond with the following reaction

$$\equiv Si_2N\text{-}NSi_2\equiv \rightarrow \equiv Si_2N\bullet + \bullet NSi_2\equiv \qquad (4)$$

The $\equiv Si_2N\bullet$ defect can be removed by re-oxidation of gate oxynitride, i.e.

$$\equiv Si_2N\bullet + O \rightarrow \equiv Si\text{-}O\text{-}Si\equiv + N \qquad (5)$$

Since the nitrogen atom and the nitrogen defect N• have the same coordination number, this replacement can occur without other atom re-arrangement (see Fig. 4).

4. CONCLUSION

The electronic structure of two-fold coordinated N atom ($\equiv Si_2N\bullet$) in different charge states in SiO_xN_y was simulated and the results indicate that this defect is an electron trap. This observation agrees with the experimental results [7]. In addition, our results also agree with Powell and Robertson [8] that the negatively charged nitrogen defect $\equiv Si_2N:$ can be a hole trap. We also rule out the possibility that the neutral $\equiv Si_2N\bullet$ defect may also act as a hole trap in Si_3N_4 which was proposed by Kirk [9]. On the other hand, simulation results also suggest that the electron localization by the $\equiv Si_2N\bullet$ defect will result in spin dissipation. This effect was experimentally observed earlier [10]. Based on the simulation results, the nature of electron traps removal during gate oxynitride reoxidation is also discussed in this work.

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