

Programming Current Enhancement by Ge Incorporation into Tunnel Oxide Film

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1. Introduction

For both the FG and the MONOS memories, higher-speed programming performance is required. In order to meet this requirement, leakage current of the tunnel oxide should be larger under high electric field, keeping its small value under low electric field for a good retention performance.

From this viewpoint, we propose a tunnel oxide having an appropriately shallow impurity level in its energy gap. As shown in Fig. 1, the shallow impurity level near the conduction band has no influence on the leakage current under the bias condition for retention, while it enhances the leakage current by trap-assisted tunneling (TAT) under the bias condition for programming. In this work, Ge ions were implanted into the tunnel oxide for the purpose of an impurity-level formation and the change in the leakage current was investigated. As a result, the enhancement of the leakage current was observed under high electric field, which shows that the Ge incorporation into the tunnel oxide is one of the promising techniques for the next-generation flash memory.

2. Samples and Experimental Procedures

The samples examined are tunnel oxides with and without Ge implantation as listed in Table I. The tunnel oxide film was formed onto an *n*-type Si monocrystal wafer and then Ge ions were implanted into the tunnel oxide for the projection range to reside within the tunnel oxide. The samples were post-annealed at 850 °C for 7.5 min or 24 min in diluted oxygen ambient.

Electrical properties were examined at room temperature for the sample having a MOS structure consisting of a *p*⁺-poly Si electrode, the tunnel oxide, and the Si substrate. The *I-V* characteristics were measured by applying a positive dc voltage to the electrode while changing its voltage value from 0 to 20 V in a stepwise manner. The *C-V* characteristics were measured at 100 kHz in order to estimate the oxide thickness T_{ox} .

3. Results and Discussion

Using the density functional theory method, the impurity levels of Si substitutionals and interstitials in alpha-quartz were calculated for several elements. The elements calculated are B, Al, P, Ge, As, and Hf, which are generally used in LSI process. Figure 2 shows the calculated Kohn-Sham level of the Ge impurity at the Si substitutional site in alpha-quartz. An unoccupied level due to Ge-O antibonding orbital is located just below the bottom of the conduction band of alpha-quartz and its relaxed electron affinity is 1.18 eV. This shallow impurity level is ex-

pected to enhance the leakage current under high electric field and improve the programming performance. In the case of other impurities, undesirable deep levels are formed irrespective of Si substitutionals or interstitials, although the calculation results are not shown here. These deep levels are considered to increase the leakage current under low electric field and deteriorate the retention performance. Therefore, Ge is found to be the most promising element among the elements calculated.

Figure 3 shows the *J-E* curves and their FN plots obtained for the samples OX (without Ge implantation) and OG1 (with Ge implantation and shorter post-annealing). The *J-E* curve for OG1 is identical to that for OX, which means that the implanted Ge atoms have no influence on the leakage current. Figure 4 shows the *J-E* curves obtained for the samples OX and OG2 (with Ge implantation and longer post-annealing). The *J-E* curves are identical at $E_{ox} < 10$ MV/cm. However, at $E_{ox} > 10$ MV/cm, the larger *J* value is achieved for OG2. Such a current enhancement only under high electric field is expected to improve the programming performance without deteriorating the reading performance such as read disturbance.

In order to investigate the reason for the current enhancement, SIMS measurement was carried out for OG1 and OG2. As shown in Fig. 5, in each sample, there are two Ge peaks: one located around the *p*⁺-poly Si/tunnel oxide interface and the other located around tunnel oxide/substrate interface. Since the Si intensity is almost constant throughout the tunnel oxide irrespective of the Ge intensity, thick $Si_xGe_{1-x}O_2$ or GeO_2 layers are unlikely to be formed in the tunnel oxide. If such $Si_xGe_{1-x}O_2$ or GeO_2 layers were formed, the *J-E* curve should be different from the one of OX at any E_{ox} values. However, the *J-E* curves for OG1 and OX are identical at all E_{ox} values. Similarly, the *J-E* curves for OG2 and OX are identical at $E_{ox} < 10$ MV/cm. This result is inimical to the existence of the $Si_xGe_{1-x}O_2$ or GeO_2 layers. Therefore, the Ge atoms can be regarded as impurities in the tunnel oxide for both OG1 and OG2. If such Ge impurities are incorporated into the Si substitutional and/or interstitial sites, impurity levels will be formed.

Next, we discuss the reason for the difference between the *J-E* curves for OG1 and OG2 at $E_{ox} > 10$ MV/cm, where the current is enhanced for OG2. There are two possibilities: one is the difference in the Ge profiles and the other is the difference in chemical states of Ge atoms. Figure 6 shows the energy diagram of OG2 at $E_{ox} = 10$ MV/cm, where the current enhancement emerges. Clearly, the current enhancement is not due to the Ge atoms around *p*⁺-poly Si/tunnel oxide interface, but due to those around

tunnel oxide/substrate interface. Since the Ge profiles of the latter interface for the two samples are in good agreement, we can eliminate the possibility of the difference in the Ge profiles. Therefore, the current enhancement is assumed to be due to the changes in the chemical state of the Ge atoms such as Si substitutionals or interstitials. If this is the case, the J - E curves obtained for OG1 and OG2 can be explained as follows: For OG2, the Ge atoms are fully oxidized as if they were incorporated in the Si-substitutional site of SiO_2 and the current is enhanced. On the other hand, for OG1, Ge oxidation is insufficient and the efficient impurity levels of Ge are not formed, resulting in no current modulation.

Finally, the J - E curve for OG2 is simulated under the above assumption. Preceding the simulation, the Ge distribution is estimated from the initial onset E_{ox} value (10 MV/cm) of the current enhancement. Using the calculated Ge impurity level of 1.18 eV and the barrier height estimated from the FN plot shown in Fig. 3, Ge is estimated to have its effective distribution around 2.0 nm from the tunnel oxide/substrate interface. This estimation is compatible with the SIMS profile shown in Fig. 5. Therefore, the J - E curve is simulated by assuming that the Ge atoms are distributed uniformly within 2.0 nm from the interface. The simulated J - E curve shown in Fig. 4 agrees well with the experimental data, assuming that the leakage current consists of both FN [1] and TAT [2] emissions. This result

suggests that the current enhancement is attributable to the Ge impurity level.

To summarize, the leakage current was enhanced under high electric field by the Ge incorporation into the tunnel oxide. The SIMS measurement and the simulation result suggest that the Ge impurity level around the tunnel oxide/substrate interface is responsible for this enhancement. The programming current enhancement induced by the Ge incorporation is expected to be one of the promising solutions for the next-generation flash memory.

4. Conclusions

Leakage current for a Ge-incorporated tunnel oxide was investigated. The leakage current was enhanced at an electric field of 10 MV/cm when the tunnel oxide was Ge-implanted and appropriately annealed. This enhancement is assumed to be due to the Ge impurity level formed at the tunnel oxide/Si substrate interface.

Acknowledgement

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References

- [1] M. Lenzlinger and E. H. Snow, J. Appl. Phys. **40**, (1969) 278.
- [2] C. Svensson and I. Lundström, J. Appl. Phys. **44**, (1973) 4657.

Table I Samples examined.

Sample	Ge ion implantation		Annealing time (min)	T_{ox} (nm)
	Voltage (keV)	Dose (cm^{-2})		
OX	-	-	7.5	7
OG1	1.0	$5.0\text{E}+13$	7.5	7
OG2	1.0	$5.0\text{E}+13$	24	9

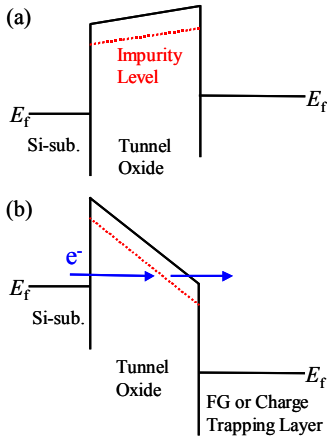


Fig. 1 Schematic energy band diagram of FG or charge trapping layer/tunnel oxide/Si substrate during retention (a) or programming (b).

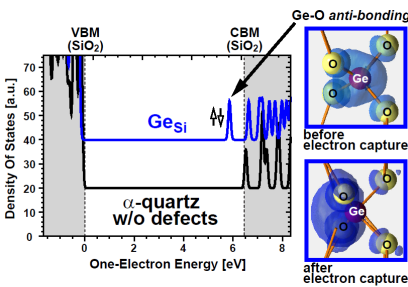


Fig. 2 Calculated Kohn-Sham levels of a substitutional Ge at a Si site in alpha-quartz.

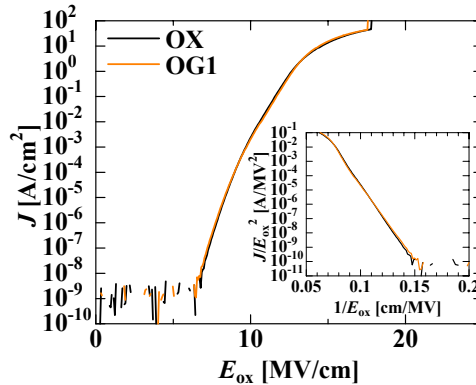


Fig. 3 J - E curves observed for OX and OG1. Inset figure shows FN plots of the J - E curves. The electric field E_{ox} is defined as $E_{\text{ox}} = (V - V_{\text{fb}}) / T_{\text{ox}}$.

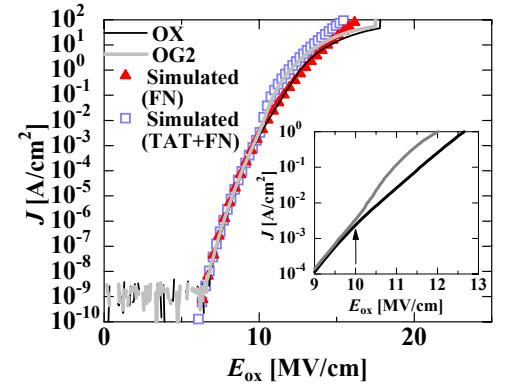


Fig. 4 J - E curves observed for OX and OG2 with simulation results. Inset figure shows an enlarged view around the onset of the current enhancement of OG2.

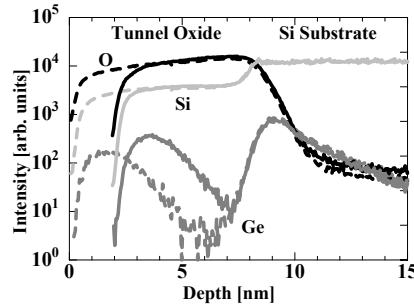


Fig. 5 SIMS profiles obtained for the samples OG1 (solid curves) and OG2 (broken curves).

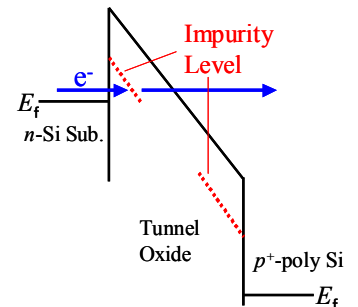


Fig. 6 Schematic energy band diagram of the sample OG2 at $E_{\text{ox}} = 10$ MV/cm.