

Defect Control in Germanium Oxide Film Thermally Grown on Germanium Substrate

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1. Introduction

Germanium dioxide has been expected to be an inter-layer between Ge-channel and high permittivity (high- κ) dielectrics for future metal-oxide-semiconductor field-effect-transistors. However, conventional GeO₂ has many problems to overcome such as thermal instability and water absorbency. It has been reported that the interface properties are deteriorated by thermal GeO volatilization due to an inter-reaction ($>420^\circ\text{C}$) between Ge and GeO₂ film [1]. Moreover, GeO₂ is soluble in water [2]. The objective of this work is to investigate the defects in the GeO₂ film which has volatile and hygroscopic natures and the mechanism controlling the defects generation.

2. Sample Preparation

GeO₂ films were formed by thermal dry oxidation of *p*-type Ge(100) substrates in furnace. For some samples, either post-oxidation anneal (POA) or post-metallization anneal (PMA) were carried out at several temperatures in N₂ ambient. HfO₂ films were deposited by reactive sputtering using Hf-metal target followed by post-deposition anneal. For electrical measurements, Al-electrodes were deposited by ex-situ thermal evaporation. Note that the oxide surface were exposed to air for a few minutes before the samples were loaded into the evaporation chamber.

3. Results and Discussion

First, the interface structure and electrical characteristics of thermally grown GeO₂ with and without GeO desorption were investigated. The chemical bonding of Ge-GeO₂ interface formed at 400 and 500°C were measured by XPS. Compared to the spectrum of 400°C oxidation, sub-oxide states such as 1+ and 3+ states are increased by oxidation at 500°C as shown in Fig. 1. This should be due to the GeO desorption during course of GeO₂ growth.

Figures 2(a) and (b) shows *C-V* characteristics of GeO₂ capacitor fabricated by thermal oxidation at 400 and 500°C, respectively. The bias was started from various negative voltages ap-

plied for each virgin sample. Although any V_{FB} dispersion were not observed in the *C-V* curve of sample oxidized at 400°C, negative ΔV_{FB} increases linearly with an increase of maximum negative gate bias in that of 500°C oxidation. This result suggests that during negative bias stressing positive charge is generated by electron emission from the oxide film. The donorlike hole-trap states should be located uniformly close to the Ge-GeO₂ interface possibly in sub-oxide layer. Only those states above the Ge Fermi-level would be positively charged. Thus, the positive charge in as-grown GeO₂ film is generated by electron emission from the hole trap which should be located in sub-oxide layer.

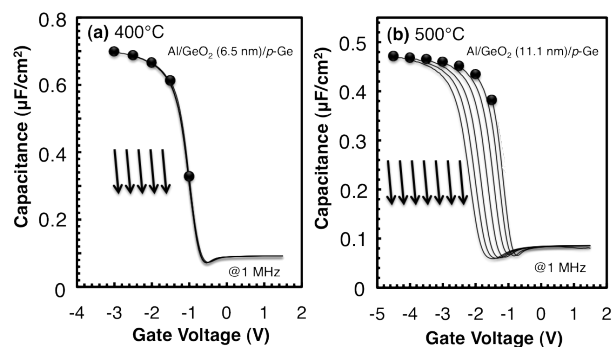


Fig. 2. *C-V* characteristics of *p*-Ge/GeO₂/Al stacks formed at 400 and 500°C measured at 1 MHz from accumulation to inversion. The circular symbols correspond to the bias starting points.

In thermally grown SiO₂ films, so-called slow-states are known to be generated by stressing and they are enhanced in the wet or water-diffused oxides [3]. To confirm the presence of water molecules in GeO₂ film, TDS analysis was carried out. Figure 3 shows TDS spectra of H₂O desorbed from as-grown samples as a function of GeO₂ thickness. Here, the samples were exposed to air for 1 hour before they were loaded into the TDS chamber. The increase of peak integral with an increase of oxide thickness indicates that water molecules desorbs not only from the GeO₂ surface but also from the bulk GeO₂.

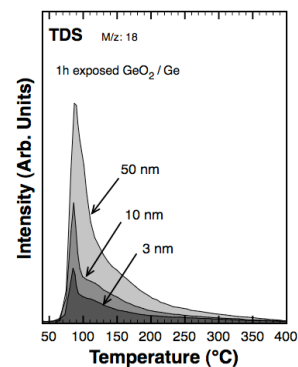


Fig. 3. TDS spectra of H₂O desorbed from GeO₂ films formed at 500°C.

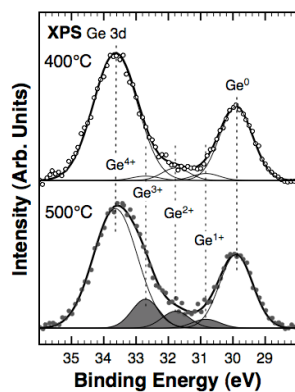


Fig. 1. XPS Ge 3d spectra of Ge/GeO₂ stacks formed by thermal oxidation at 400 and 500°C.

In order to investigate the relation between the donor-like traps and water molecule in the oxide film, 10-nm-thick as-grown samples formed at 500°C were exposed to air at room temperature for several hours before Al gate electrode formation to diffuse the moisture from air ambient into GeO₂ layer. Figure 4(a) shows ΔV_{FB} plotted as a function of maximum oxide field applied by negative gate bias. Data of both as-grown sample, which corresponds to the data of Fig. 2(b), and a sample exposed to the atmosphere for 100 hours after Al electrode formation are also shown as references. The slope of the fitting lines, which corresponds to the density of the donorlike traps distributed energetically uniformly in the oxide film near the valence-band-edge of Ge, is increased with an increase of the air exposure time. This result indicates that water molecules, which create the donorlike traps, were absorbed into the GeO₂ film during the exposure. In addition, there are almost no changes of ΔV_{FB} dispersion in the sample exposed to the atmosphere for 100 hours after Al electrode formation compared to as-grown sample. This suggests that the Al electrode would prevent the absorption of the water molecules into the GeO₂ film.

Here, to investigate the effects of the amount of water molecules in the oxide on the charge generation, PMA was carried out. Samples were annealed in N₂ ambient at various temperatures after the Al electrode formation. As a reference, POA sample was also fabricated. Figure 4(b) shows ΔV_{FB} plotted as a function of maximum oxide field applied by negative gate biases as same as Fig. 4(a). Comparisons were made by PMA temperatures and between PMA and POA at 300°C. The results clearly show that ΔV_{FB} dispersions are reduced with an increase of PMA temperature. The dispersion are almost completely eliminated by PMA at 300°C. Moreover, POA has no effects on the ΔV_{FB} . These results suggest that even though there are Al electrodes on the GeO₂ film, water molecules present in the GeO₂ below the Al electrode which causes hole traps desorbed from the GeO₂-Al side-edge during the anneal. After the annealing, the Al film would prevent further absorption of water molecules into the GeO₂ under atmospheric conditions at room temperature. Thus, once metal

electrode is formed, water desorption and absorption behaves irreversibly by a cycle of anneals and air exposure. On the contrary, POA has no effect on ΔV_{FB} because the water molecules can be desorbed and absorbed reversibly before the Al electrode formation. In this way, the total number of the positive charge can be controlled by amount of water molecules present in the GeO₂ film.

Finally, for high- κ dielectrics formation on GeO₂ as an inter-layer, PDA was carried out for water desorption. Here, HfO₂ film (~10 nm) was deposited on GeO₂ film (~10 nm) formed at 500°C, followed by PDA at 350°C in N₂. C-V characteristics of the *p*-Ge/GeO₂/HfO₂ structure are shown in Fig. 5. The V_{FB} dispersion, which observed in the *p*-Ge/GeO₂ stack as shown in Fig. 2(b), was drastically improved after the PDA. This suggests that water molecules existed in the Ge sub-oxide layer were desorbed by the PDA and HfO₂ film played a role of a passivation layer for water absorption into GeO₂ inter-layer.

3. Conclusions

It has been investigated that the nature of anomalous positive charge in the GeO₂ film as well as of its generation mechanism. Positive charge in the GeO₂ film is generated by electron emission from water-related donorlike traps above Ge Fermi-level and increases linearly with the maximum field in the oxide. Moreover, it is found that the positive charge can be controlled by amount of water molecules in the oxide film. PDA is effective for water desorption in the high- κ /Ge formation process.

Acknowledgements

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References

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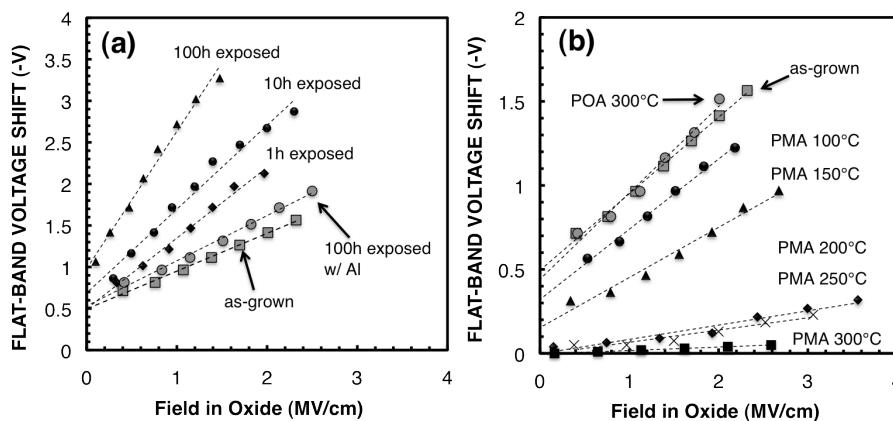


Fig. 4. Flat-band voltage shift vs. maximum oxide field applied by negative gate bias as the function of (a) air exposure time and (b) PMA temperature.

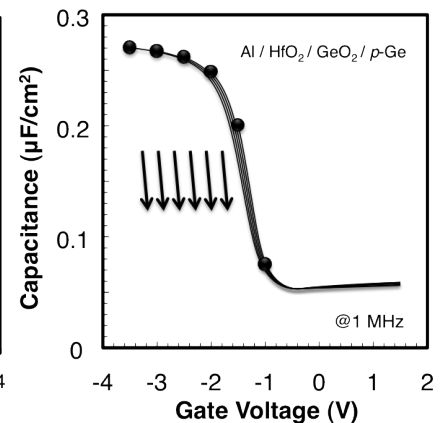


Fig. 5. C-V characteristics of *p*-Ge/GeO₂/HfO₂/Al capacitor.