

Thermodynamic consideration and experimental demonstration for solving the problems of GeO₂ solubility in H₂O and GeO desorption from GeO₂/Ge

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Abstract

The water solubility and thermal instability of GeO₂ are attributable to the intrinsic property of the weak GeO₂ network. We found Y doping increases the hygroscopic tolerance and thermal stability by strengthening the network of GeO₂, thereby improving the electrical properties of Ge/GeO₂ stack. Those properties are discussed from the thermodynamic points of view.

1. Introduction

Similar to Si/SiO₂, GeO₂ is regarded as one of the best candidates for the passivation of Ge as interfacial layer (IL) between Ge and high-*k* [1-3]. However, there are two major disadvantages in GeO₂ comparing to Si/SiO₂, namely, the water solubility and thermal instability. These inevitably cause problems in Ge-based device process as well as the reliability issues. In this work, we discuss that both are derived from a same origin thermodynamically, and a solution of one will also be that of the other one. As an example, we pick yttrium doping into GeO₂ (Y-GeO₂) from the thermodynamic viewpoint as well as experimental demonstration. In addition, electrical properties of Ge/Y-GeO₂ gate stack are also shown.

2. Experimental details

Various thicknesses (2 to 11 nm) of Y-GeO₂ were deposited on Ge by co-sputtering of Y₂O₃ and GeO₂. For comparison, same thicknesses of pure GeO₂ were also deposited on Ge by sputtering. Post deposition annealing was carried out at 500 °C in N₂ for 30 sec. The Y atomic percentage in Y-GeO₂ was controlled to be 10% (Y/Ge=1/9) or 30% (Y/Ge=3/7) by sputtering power and confirmed by XPS measurements of Ge 3*d* and Y 3*d* core level spectra. The etching rate was estimated by XPS after immersion into deionized water. Thermal desorption spectrum (TDS) was used to measure the GeO desorption feature of Ge/Y-GeO₂ stacks. To study electrical properties of Ge/Y-GeO₂ stacks, Au and Al were deposited by vacuum evaporation for the gate electrode and substrate contact of MOSCAPs, respectively, and the capacitance-voltage (*C-V*) and current-voltage (*I-V*) characteristics were measured at room temperature (RT).

3. Results and Discussion

The water solubility is the most obvious difference

between GeO₂ and SiO₂. This might be phenomenologically explained by the weaker network of GeO₂. However, the slightly Y doping can strongly influence the water solubility of GeO₂. Fig. 1 shows the Y-GeO₂ and GeO₂ thickness estimated by XPS as a function of immersion time in pure deionized water. 7 nm of GeO₂ completely dissolves in water immediately, while the etching rate of Y-GeO₂ is drastically decreased. Y is expected to strengthen the GeO₂ network, thereby reduces the reaction of GeO₂ with water-related species.

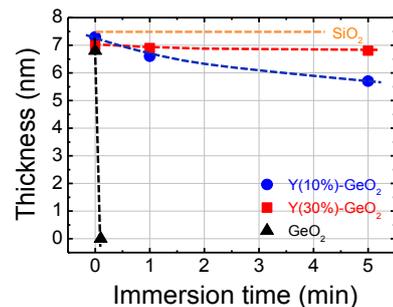


Fig. 1 Thickness of Y-GeO₂ and GeO₂ as a function of immersion time in pure deionized water. Note that SiO₂ is insoluble in water.

This prominent effect of Y is also reflected in the higher thermal stability of Y-GeO₂. Fig. 2(a) shows the TDS peak temperature corresponding to GeO (M/z=90) as a function of initial Y-GeO₂ thickness. The desorption of GeO from Ge/GeO₂ [4] and SiO from Si/SiO₂ [5] are also shown for comparison. Ge/Y-GeO₂ stack shows higher GeO desorption temperature than Ge/GeO₂ stack for each thickness of respective films. With increasing Y doping, GeO desorption behavior of Y-GeO₂ is getting closer to the

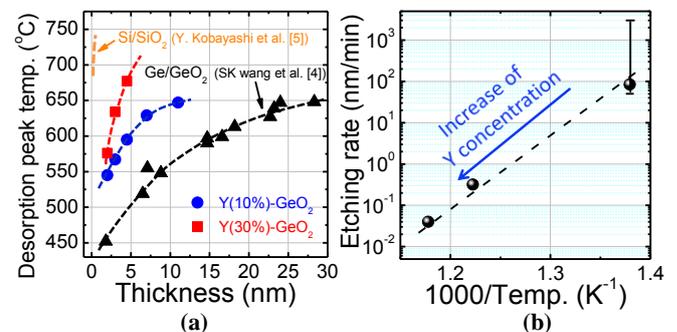


Fig. 2 (a) GeO desorption peak temperature of Ge/Y-GeO₂ stacks as a function of Y-GeO₂ thickness. The desorption peaks of Ge/GeO₂ and Si/SiO₂ stacks are also shown for comparison. (b) Correlation between desorption temperature and etching rate.

Si/SiO₂ case. **Fig. 2(b)** shows an obvious correlation between etching rate and desorption peak temperature. This correlation is originated from their common dependence on the strength of GeO₂ network, which increases with Y doping.

The oxygen vacancy (V_O) formation at Ge/GeO₂ interface and diffusion through GeO₂ bulk have been proposed to be the dominate mechanisms for GeO desorption [5]. To clarify the influences of Y on the V_O formation and diffusion in Ge/GeO₂ stack, bilayer stacks were deposited as schematically shown in **Fig. 3(a)**. The Y was doped in different positions of the GeO₂ layer, namely, bottom Y-GeO₂ (Ge/Y(10%)-GeO₂/GeO₂) and top Y-GeO₂ (Ge/GeO₂/Y(10%)-GeO₂), while the total thickness of the bilayer was fixed at 12 nm. TDS spectra of GeO desorption from these bilayer stacks are shown in **Fig. 3(b)** together with the spectrum of a Ge/GeO₂ (12 nm) stack. As we expected, the desorption temperatures of both bilayer stacks are higher than that of Ge/GeO₂ stack, while the desorption temperature of the two bilayer stacks are almost the same regardless of the different positions of Y-GeO₂. Thereby we conclude that the suppression of GeO desorption can be mainly attributed to the limiting of V_O diffusion in Y-GeO₂.

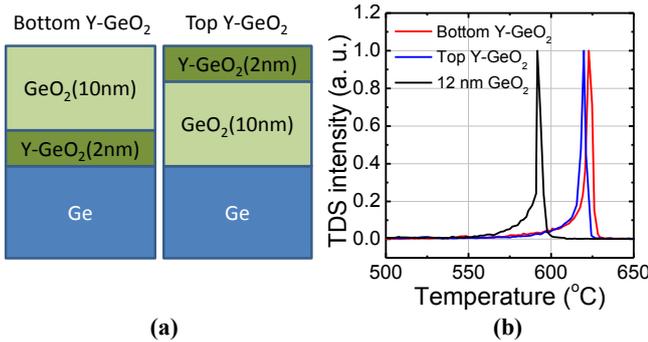


Fig. 3(a) Schematic of bilayer stacks with bottom and top Y-GeO₂. **(b)** Corresponding GeO desorption spectra. The spectrum of a 12 nm Ge/GeO₂ stack is also shown.

By suppressing the GeO desorption, Y doping in GeO₂ is expected to improve both the interface and bulk properties of Ge/GeO₂ stack. **Fig. 4(a)** shows bidirectional $C-V$ curves of Au/Y(10%)-GeO₂/Ge MOSCAPs measured at RT. The physical thickness of Y-GeO₂ is 3 nm and EOT is estimated to be 1.45 nm ($k \sim 8$). No hysteresis or frequency dispersion is observed, indicating an extremely low interface states density. The poor 1MHz $C-V$ curve of a Ge/GeO₂ stack with same physical thickness (thicker EOT) is also shown for comparison. **Fig. 4(b)** shows the gate leakage current as a function of physical thickness of GeO₂ or Y-GeO₂. The leakage currents in Ge/Y-GeO₂ stacks are significantly decreased comparing to Ge/GeO₂ stacks, indicating that the bulk defects are drastically reduced by the suppression of V_O diffusion. It is noticed, however, that the leakage current of Ge/Y-GeO₂ stack increases with an increasing of Y concentration from 10 to 30%, indicating that an alternative leakage path might be formed by the excessive Y doping. Since the localized structures revealed by water etching are observed in AFM images (data not shown), it is likely that 30% of Y doping deteriorates the uniformity of the Y-GeO₂.

The leakage through the boundary of these localized structures explains the leakage current increase.

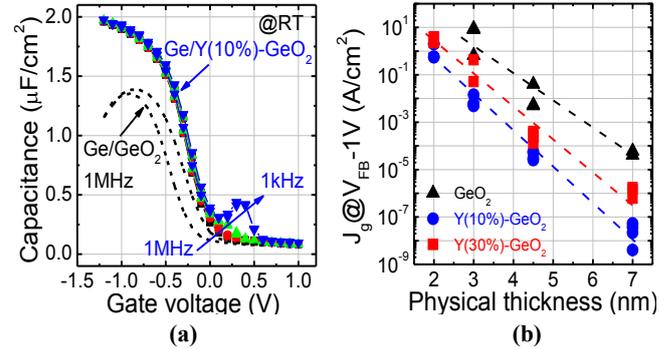


Fig. 4(a) Bidirectional $C-V$ curves of Au/Y(10%)-GeO₂/Ge MOSCAPs measured at room temperature. The $C-V$ curve of Ge/GeO₂ is also shown for comparison (dotted line). **(b)** Leakage currents of Ge/Y-GeO₂ and Ge/GeO₂ stacks as a function of the physical thickness.

We propose that the weak network of GeO₂ is the common reason for GeO₂ water solubility and thermal instability. The remarkable effect of Y on GeO₂ can be summarized as the increasing of average dissociation energy of metal-oxygen bonds in GeO₂ network, which increases the Gibbs free energy of reactions related to the water dissolution and GeO desorption as shown in **Figs. 5(a)** and **(b)** respectively.

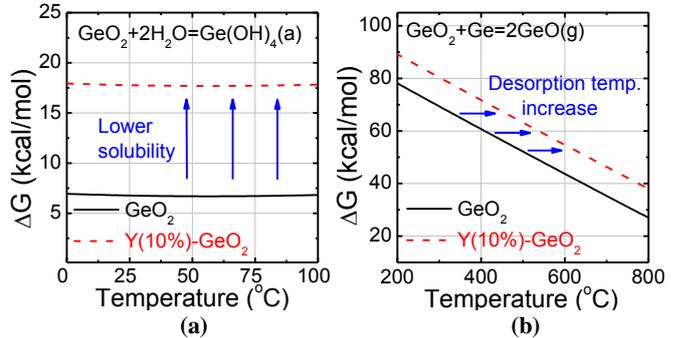


Fig. 5 Y doping effect on the Gibbs free energy of the reactions related to **(a)** GeO₂ dissolves in water. **(b)** GeO desorption from Ge/GeO₂ stack (from HSC database).

4. Conclusion

Y doping into GeO₂ provides both stronger resistance to water and better thermal stability against GeO desorption. Those are well understandable from thermodynamic viewpoint that the Gibbs free energy of both reactions increases with Y doping. The suppression of desorption provided valid interface passivation with low interface states and leakage current. The increase of k is also beneficial to the EOT scaling. However, high Y concentration causes the non-uniformity of Y-GeO₂, which increases the leakage current.

Reference

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