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Origin of Self-limiting Oxidation of Ge in High-Pressure O_2 at Low Temperature

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Abstract

The self-limiting oxidation of Ge by low temperature high-pressure oxidation (LT-HPO) is discussed from the viewpoint of the GeO_2/Ge interface strain induced by thermal oxidation. The interface strain in Ge after LT-HPO is investigated by Raman spectroscopy, and the physical origin of the retarded oxidation rate of Ge in LT-HPO is discussed.

1. Introduction

We have already demonstrated superior properties of pure GeO_2/Ge gate stacks formed by high-pressure oxidation (HPO) [1]. An obvious disadvantage of this process, however, is that relatively thick GeO_2 is necessarily formed. We have recently found that the retarded oxidation rate of Ge occurs in HPO with slightly lower oxidation temperature, resulting that both ultra-thin GeO_2 and high quality GeO_2/Ge interface can be achieved [2]. We call it as low temperature high-pressure oxidation (LT-HPO). Furthermore, the layer-by-layer oxidation [3] in Ge was observed by oxidizing the atomically flat Ge surface [4] with LT-HPO. Both properties are quite beneficial for Ge MOSFETs with very thin GeO_2 together very high electron mobility at high inversion carrier density region [5].

In this paper, we report GeO_2/Ge interface strain after thermal oxidation. The self-limiting Ge oxidation is discussed from the viewpoints of GeO_2/Ge interface strain induced by LT-HPO, by using Raman spectroscopy measurement, which is a powerful method for strain analysis [6].

2. Experimental Details

p-type Ge(100) and (111) wafers with resistivity of 0.5 Ω cm were used in this study. HPO was carried out in a specialized furnace in wide ranges of temperatures and P_{O2}. Note that P_{O2} in this work is defined at room temperature before increasing the furnace temperature. HPO and LT-HPO were carried out at 550°C and 500°C in the same P_{O2} of 70 atm. The thickness of GeO_2 film was accurately determined by combined measurements of grazing incidence X-ray reflectivity with spectroscopic ellipsometry. The GeO_2/Ge interface strain was evaluated by Raman spectroscopy with λ = 488 nm of Ar ion laser and λ = 325 nm of HeCd laser, respectively.

3. Results and Discussion

We focus that the oxidation rate of Ge is reduced as P_{O2} increases below 520°C, as shown in **Fig. 1** [2]. We first consider the diffusion-limited model, where the oxidant diffusivity might be increased in GeO_2 grown by LT-HPO. To clearly see the oxygen diffusion behavior in GeO_2 film, the same thickness of GeO_2 on Ge was prepared by atmospheric-pressure oxidation (APO) and LT-HPO, respectively. **Fig. 2** shows the additional growth of GeO_2 film in two GeO_2/Ge stacks as a function of oxidation time under P_{O2} of 1 atm. No thickness difference between APO and LT-HPO grown GeO_2 films is observed, which suggests that the retarded oxidation rate of Ge in LT-HPO is not due to the oxidant diffusion.

If one were to assume that LT-HPO in Ge is interface-reaction-limited, the oxidation rate should be mainly controlled by GeO_2/Ge interface strain level. Since the retarded oxidation rate of Ge was only observed in LT-HPO, the interface strain was first estimated by Raman spectroscopy with λ = 488 nm, corresponding to approximately 19 nm of the penetration depth (l) into Ge substrate. **Fig. 3(a)** and **(b)** show the histogram of stress distribution in Ge substrate measured at 128 points over 8x8 μm^2 for the GeO_2/Ge interface formed in LT-HPO (500°C) and HPO (550°C), respectively. The stress-free Ge substrate was used for the reference of Raman peak shift. It is found that a larger tensile strain in Ge is observed from the GeO_2/Ge interface formed in LT-HPO. To more clearly observe the GeO_2/Ge interface strain, HeCd laser with λ = 325 nm was used in Raman spectroscopy. Note that the penetration depth into Ge in this case is a few nm, and thus it should be more sensitive to acquire GeO_2/Ge interface strain information. **Fig. 4** shows typical Raman spectra for GeO_2/Ge stacks grown by HPO and LT-HPO in addition to reference Ge. The clear strain difference of GeO_2/Ge interface among three samples was observed. Although GeO_2 thickness is different from each other, such a big difference should be due to the oxidation condition difference. **Fig. 5** shows the histogram of interface strain distribution in Ge which was evaluated by HeCd laser. There are two interesting results in Fig. 5. One is that the distribution is much wider than the results in Fig. 3. The other is that there are both tensile and compressive strains only in the case of LT-HPO.

From the results in Figs. 2-5, the retarded oxidation rate of Ge in LT-HPO is likely to be attributable to the interface strain. Although apparent effect is quite similar to the self-limiting oxidation observed in Si nano-structures [7], this is the case simply for the planar oxidation. Interestingly, discontinuities at the SiO_2/Si and GeO_2/Ge interfaces are very similar from the viewpoint of atomic bonding configuration. Si-Si bond length in Si is 0.235 nm and the Si-Si 2nd neighbor distance in SiO_2 is 0.305 nm, while Ge-Ge bond length in Ge is 0.244 nm and the Ge-Ge 2nd neighbor distance in GeO_2 is 0.31 nm [8]. The molar volume mismatch of SiO_2 and Si is about 220% and that of GeO_2 and Ge is about 210%. On the other hand, it is expected by the first principle calculation that Ge atom will not be emitted from Ge substrate to GeO_2 [9]. In addition, HPO can definitely suppress GeO desorption during oxidation [10], resulting that a large density of Ge atoms are accumulated at the interface and the oxidation proceeds with extremely low oxidation rate. In addition, no viscous flow is expected at low temperature.

From the Raman results in Fig. 3 and 5, the strain distribution in Ge is schematically depicted as shown in **Fig. 6**. With approaching to the interface, the compressive stress increases to suppress the oxidation [11], while the tensile stress increases deeper inside Ge substrate. The compressive one is derived from the oxidation mentioned above and the tensile one might be from the macroscopic volume expansion in the oxidation.

4. Conclusion

The origin of self-limiting oxidation in Ge by LT-HPO was studied by Raman spectroscopy. The larger strain in Ge substrate is observed for GeO_2/Ge interface formed in LT-HPO. The retarded oxidation rate of Ge in LT-HPO is attributable to the interface compressive strain in Ge.

References

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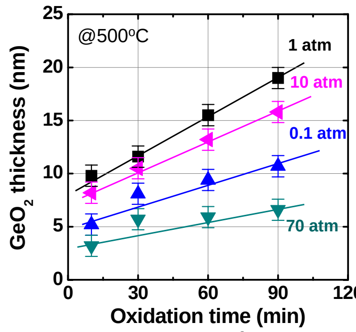


Fig. 1 Oxidation time dependence of GeO_2 thickness at 500°C as a parameter of P_{O2} [2]. The oxidation rate is reduced as P_{O2} increases below 520°C.

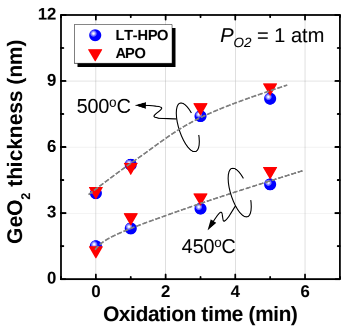
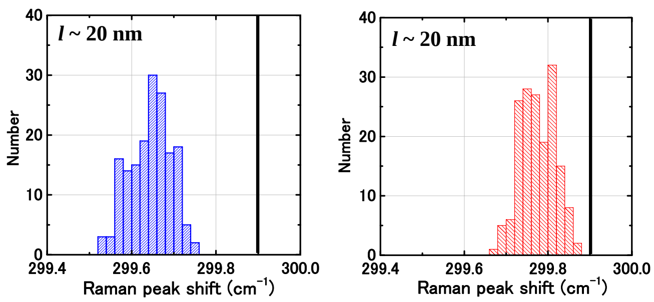


Fig. 2 Additional growth of GeO_2 film in two GeO_2/Ge(111) stacks as a function of oxidation time under P_{O2} of 1 atm. The same thickness of GeO_2 on Ge was prepared by APO and LT-HPO, respectively. No difference of additional oxidation between APO and LT-HPO grown GeO_2 films is observed.



(a) (b)

Fig. 3 Histogram of strain distribution in Ge substrate measured at 128 points over 8x8 μm^2 for the GeO_2/Ge(111) interface formed in **(a)** LT-HPO (500°C) and **(b)** HPO (550°C), measured by Raman spectroscopy with λ = 488 nm.

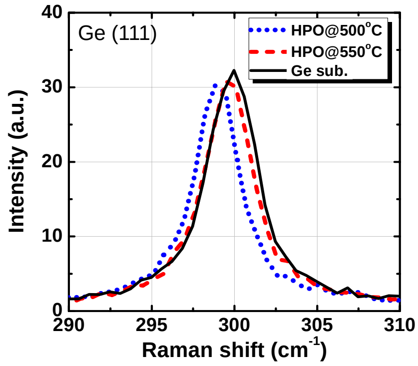
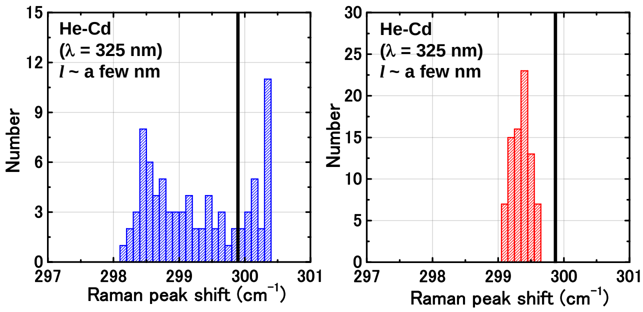


Fig. 4 Raman spectra for GeO_2/Ge(111) stacks grown by HPO and LT-HPO. The Ge substrate before thermal oxidation was plotted together for comparison. To more clearly observe the GeO_2/Ge interface strain induced by LT-HPO, we used ultraviolet Raman spectroscopy with λ = 325 nm of HeCd ion laser. The clear strain difference of GeO_2/Ge interface among three samples was observed.



(a) (b)

Fig. 5 Histogram of interface stress distribution in Ge substrate for the GeO_2/Ge(111) interface formed in **(a)** LT-HPO and **(b)** HPO. The interface stress was evaluated by HeCd ion laser. There are two interesting results. One is that the distribution is much wider than the results in Fig. 3. The other is that there are both tensile and compressive strains only in the case of LT-HPO.

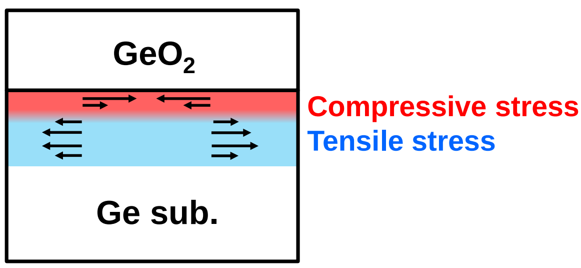


Fig. 6 Schematic image of the strain distribution at the GeO_2/Ge interface. Just at the interface, the compressive stress is expected, while in Ge deeper inside, the tensile strain is distributed, based on the Raman result in Fig. 3 and 5. The compressive stress at the GeO_2/Ge interface (or transition region in GeO_x) may stop the oxidation in LT-HPO.