

TO- and LO-mode analyses in asymmetric stretching vibrations in ultra thin thermally grown GeO₂ on Ge substrate

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1. Introduction

It was demonstrated that high-performance Ge MISFETs with GeO₂ for a gate dielectric was achievable by overcoming thermodynamically unstable nature of Ge oxides, where suppressing GeO desorption with high oxygen pressure oxidation (HPO) played a key role [1]. Yet controlling thermodynamic parameters such as temperature and pressure enables almost defect-free bulk and interface, there still remains uncertainty in the GeO₂ network structure [2]. It is well-known fact that Si/SiO₂ interface has about 1 nm-thick transition region where the infrared (IR) absorption band due to optical phonon associated with Si-O-Si asymmetric stretching vibrations shifts to the lower frequency. This fact is considered to originate from sub-oxides [3] and/or built-in stress [4] at SiO₂/Si interface. In this paper, we report the IR absorption in GeO₂ structure to understand how the ultra-thin GeO₂ film structure is.

2. Experimental

The GeO₂ films were grown on cleaned (100) p-Ge wafers by atmospheric pressure oxidation (APO) and HPO, conditions, and then successively etched back by the mixture of water and methanol. Backside oxides of the Ge wafers were removed by H₂O-dipped Q-tip. Homogeneous etching was confirmed by AFM images. Fourier transform infrared spectroscopy (FTIR) measurements were performed, with both perpendicular (0°) and oblique (65°) angle at a resolution of 4.0 cm⁻¹, in a vacuum. The peak positions of both transverse optical (TO) and longitudinal optical (LO) phonon modes associated with Ge-O-Ge asymmetric stretching vibrations, were measured. GeO₂ thickness was estimated by spectroscopic ellipsometry.

3. Results and Discussion

Fig. 1 shows film thickness change with etching time. Etching rate gradually turns to be slower as oxide thickness decreases, which suggests an existence of denser region thinner than ~3 nm. Both transmittance spectra of APO and HPO samples are shown in **Fig. 2**. Two important facts are noticed. One is that TO peaks of both samples slightly red-shift with the oxide thickness decrease, and the other is that LO peak is significantly different from each other.

Both TO and LO peak position are plotted as a function of oxide thicknesses as shown in **Fig. 3(a)** and **(b)**, respectively. Only a slight difference of the peak position is observed between APO and HPO grown GeO₂ films at 550 °C, while APO one at 450 °C noticeably starts to shift to lower wave number from thicker film than those at 550 °C.

According to the central force model [5], the TO mode is almost dominated by the average Ge-O-Ge bridging bond angle θ , as shown in the following equation ;

$$\nu_{TO} = \frac{1}{2\pi} \sqrt{\frac{\alpha \cdot \sin^2(\theta/2) + \beta \cdot \cos^2(\theta/2)}{m_o}}$$

where α : central force constant, β : non-central force constant and m_o : oxygen mass, respectively.

Thus, we can consider this red-shift below 5 nm as the decrease of Ge-O-Ge bond angle θ in GeO₂ network, due to the same origin as SiO₂ case. Although other causes bringing about the TO-peak shift might be possible, for example, the geometrical effect [6], it is not likely the case. Thus, we can conclude that higher oxidation temperature can reduce GeO₂ transition layer thickness.

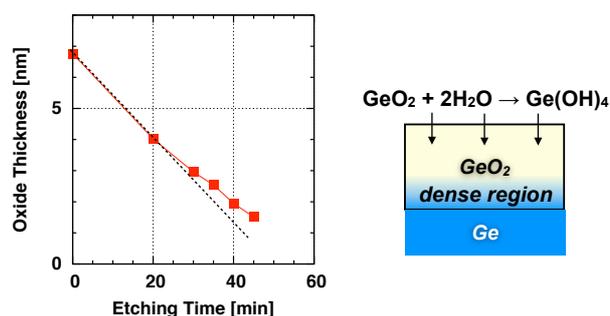


Fig. 1 Ge oxide thickness vs. Etching time. Etching by H₂O diluted with methanol (1 : 60) was performed for GeO₂ film grown at 550 °C. Etching rate was gradually slowed as oxide thickness decreases, which indicates that the densified region exists below ~3 nm.

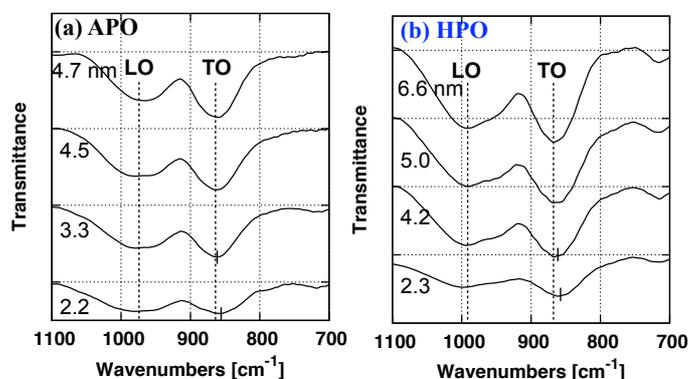


Fig. 2 Transmittance spectra of oblique incidence beam, observed in successively etched back GeO₂ films. TO bands of both APO and HPO samples slightly shift to red with decrease of thickness. LO bands appear at considerably different positions. Subtle peaks appearing both samples at ~ 710 cm⁻¹ might come from the vibration of Ge-OH [7].

On the other hand, it is surprising that LO peaks have significantly large dependences on both oxidation temperature and O_2 pressure, and are not sensitive to the oxide thickness below 5 nm.

By using TO peak position ν_{TO} , LO peak position ν_{LO} can be expressed as ;

$$\nu_{LO} = \sqrt{\nu_{TO}^2(\theta) + C\rho Z^2}$$

where it depends not only on the bond angle θ but also on the mass density ρ as well as the effective charge Z . Since we cannot see clear thickness dependence of LO modes below ~ 5 nm, LO mode vibration should be predominantly determined by ρ and Z rather than θ . The effective charge Z contribution to LO mode is not likely to be a significant at ~ 5 nm, because it should change the TO mode as well. Thus, the increase of LO-TO peak difference at ~ 5 nm reflects the macroscopic densification of the film.

Furthermore, **Fig. 3** shows that thick HPO and APO

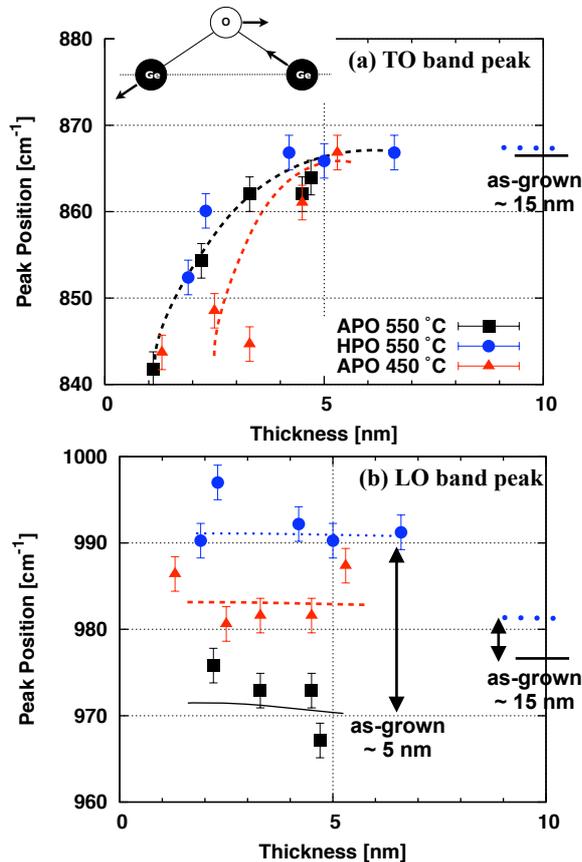


Fig. 3 (a) TO and (b) LO absorption peak positions vs. Ge-oxide thickness. GeO₂ was grown in APO (1 atm) at 550 °C (■), HPO (80 atm) at 550 °C (●) and APO at 450 °C (▲). TO peak positions were determined from spectra obtained by 0° beam and those of LO from spectra by 65° beam. Temperature dependence of TO peaks was clearly observed in (a). From (b), both temperature and pO_2 dependence of LO peaks are significant in ultra-thin region, while relatively thicker films (~ 15 nm) show less difference on pO_2 , as demonstrated by the difference between two arrows.

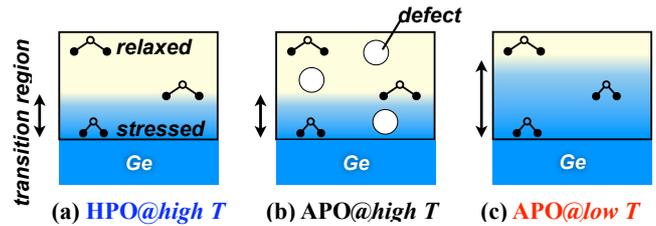


Fig. 4 Schematic of GeO₂ structures for (a) HPO at high temperature, (b) APO at high temp. and (c) APO at low temp., respectively. Grown at low temperature, film has the long transition region including stress. As temperature increases, this stress is released and the transition region becomes shorter, nonetheless a lot of macroscopic defects are generated due to GeO desorption. However, by applying high pO_2 , this GeO desorption can be suppressed consequently to form dense and stress-free structure.

GeO₂ (~ 15 nm) have the same saturated TO mode value. Concerning LO modes, it is of interest that a big difference of LO modes between APO and HPO grown GeO₂ (~ 5 nm) is reduced very much in thicker GeO₂ region. Such a large separating of LO mode vibrations among several GeO₂ growth conditions should be unique to ultra-thin GeO₂ film. GeO₂ thickness is the thicker, the GeO₂ film is the farther from the interface. Namely, the interface reaction can less affect the quality of GeO₂ in thicker region.

Finally we consider the dependency of GeO₂ structure on two parameters, pO_2 and temperature, as schematically shown in **Fig. 4**. In HPO at high temperature condition, less GeO desorption at higher pO_2 can grow quite robust and dense GeO₂ film. In APO at high temperature, more GeO desorption may cause defects like voids, reducing the film density, although the local bond structure is the same as that in HPO case. In APO at lower temperature condition, the local structure is significantly unrelaxed.

4. Conclusion

A thorough IR investigation of thin GeO₂ was performed for the first time, with a special conscious of both TO and LO modes. Local bond feature such as the bridging bond angle is governed by the oxidation temperature just like that in SiO₂, while macroscopic one such as void defect seems to be determined by both temperature and pO_2 , particularly below ~ 5 nm. This is characteristic for GeO₂ and has not been concerned in SiO₂ / Si system. This point must be taken into account for the future gate stack design of Ge-MISFETs.

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