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Spectroscopic Ellipsometry Study on Defects Generation in GeO_2/Ge stacks

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1. Introduction

It is required to control the properties of Ge/dielectric interfaces precisely to realize high-performance Ge MISFETs, however, the thermodynamically unstable nature of Ge native oxides [1, 2] has been a big issue to overcome. It is reported that the GeO volatilization is caused by the GeO_2/Ge interface reaction, and that volatilization is the origin of the deterioration of GeO_2/Ge MIS characteristics [2]. We have already reported that spectroscopic ellipsometry (SE) measurement is a powerful method to clarify the defects in GeO_2/Ge stacks [3]. In this study, the defect states generation in GeO_2 films was further investigated by using SE measurements.

2. Experimental

The GeO_2 films were deposited by rf-sputtering of GeO_2 target on HF-treated Ge (100) wafers, followed by the annealing in N_2 or O_2 ambient at 500 - 700°C. The refractive indices (n) and extinction coefficients (k) of GeO_2 films were evaluated with SE, by assuming the model with a single layer on the substrate. The "point-by-point" calculation at each wavelength [3] was employed, without assuming any dielectric functions for GeO_2.

3. Results and Discussions

The spectra of n of sputtered GeO_2 films do not change significantly, however, those of k change dramatically by N_2 annealing [3]. The spectra of k are shown as a function of photon energy in **Fig. 1**, for the films annealed in N_2 at 600°C for various annealing time. The as-sputtered film shows a sharp increase of k at ~ 6 eV, which corresponds to the bandgap of GeO_2, however, a gradual increase of k in the region of 5 - 6 eV emerges after annealing. This sub-gap photo-absorption will be attributed to a generation of significant density of defect states. The emergence of the two peaks at ~5.1 eV and ~5.8 eV in the spectra suggest the generation of two kinds of defect states simultaneously in the deteriorated GeO_2 films.

Next, k spectra of bi-layered GeO_2 films, consisting of annealed and non-annealed (fresh) layers, were investigated in order to distinguish whether those sub-gap defects are bulk defects in GeO_2 or interface defects at GeO_2/Ge. The 1st deteriorated layers with different thicknesses were prepared by N_2 annealing at 600°C, followed by the deposition of the 2nd fresh layers to attain a common total thickness, as depicted in **Fig. 2**. The k values at 5.1 eV and 5.8 eV of those four samples are plotted in **Fig. 3**, which clearly shows that the amount of sub-gap defects is proportional to the thickness ratio of annealed layer to the total layer. Thus the observed defects by SE measurements are not the defects formed at GeO_2/Ge interface, but the bulk defects uniformly existing in the annealed film.

Next, the relationship between the sub-gap defects generation with GeO volatilization was investigated. In **Fig. 4 (a)** and **(b)**, the k values at 5.1 eV and 5.8 eV of the films

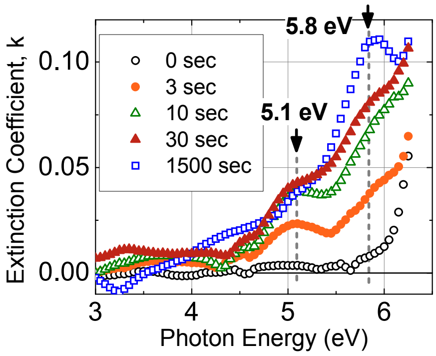

Fig.1 Extinction coefficient (k) of GeO_2 films annealed at 600°C for various time evaluated by spectroscopic ellipsometry. Sub-gap photo-absorption increases in the energy region below the bandgap energy (~6.1eV) by annealing. The emergence of two peaks at ~5.1eV and ~5.8eV correspond to the generation of two kinds of defect states in GeO_2 films.

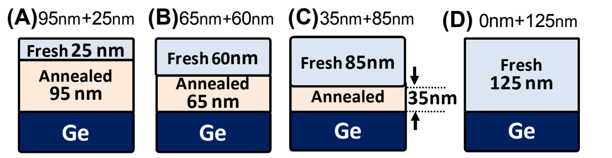

Fig.2 Schematic of samples (A)-(D) with GeO_2 bi-layers. The 1st layers (annealed) with different thicknesses (95, 65, and 35 nm) were prepared by annealing sputtered films at 600°C in N_2, followed by the deposition of the 2nd layers (fresh). The thicknesses of the 2nd layers were controlled to obtain a common total thickness (120~125 nm). The ratios of the annealed layer thickness to the total (annealed + fresh) thickness are: (A) 0.76, (B) 0.52, (C) 0.29, and (D) 0, respectively. The sample (D) consists only of 2nd (fresh) layer.

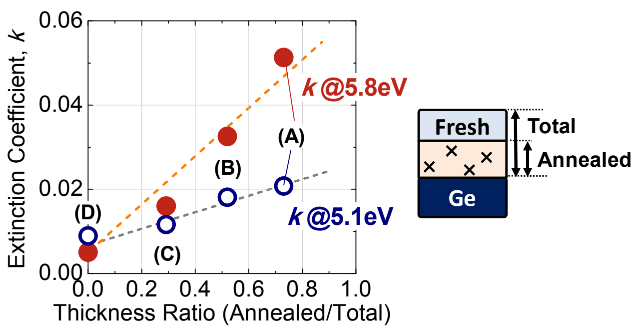

Fig.3 Extinction coefficient (k) values at 5.1 eV and 5.8 eV for the GeO_2 bi-layers (A) ~ (D) depicted in Fig.2, as a function of the ratio of the annealed layer thickness to the total thickness. By increasing the annealed/total thickness ratio, the intensity of sub-gap absorption increases, which clearly indicates that the sub-gap states are attributable to the bulk defects in deteriorated GeO_2 layers, rather than the interface defects at GeO_2/Ge.

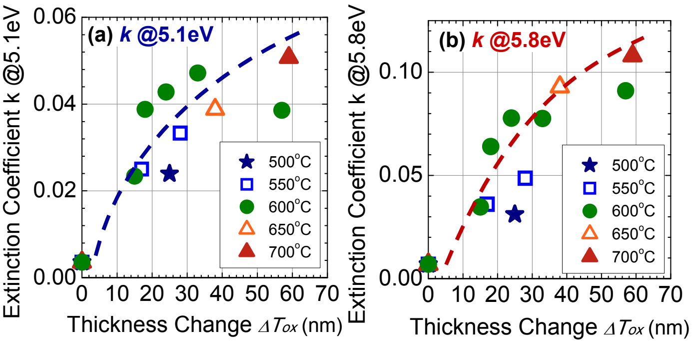

Fig. 4 Relationship between the change of the film thickness by GeO volatilization and the sub-gap defects generation, which is corresponding to the increase of the extinction coefficients (k) at **(a)** 5.1 eV and **(b)** 5.8 eV. The amount of GeO volatilization determines the generated defect density, irrespective of annealing temperature and time.

annealed at 500°C - 700°C for various time, are plotted as a function of thickness change (ΔT_{ox}) by annealing. It should be noted that the sub-gap defect density seems to be described as a function of the amount of GeO volatilized from the film, irrespective of the annealing temperature, or annealing time. In addition, the fact that the k spectrum of the GeO_2 film deposited on surface-oxidized Si (100) wafer does not show any sub-gap photo-absorption even after annealing at 650°C [3] also supports our consideration, because it is reported the GeO volatilization does not occur from the GeO_2 films deposited on surface-oxidized Si substrate in this temperature range [2].

It has been reported that oxygen deficient GeO_2 bulk glass shows a UV-absorption band at ~ 5 eV [4]. From theoretical and experimental studies, this absorption band is considered to be attributable to Ge^{2+} defects or oxygen vacancies [4,5]. It should be noted that the energy regions of these defects are quite coincident with what we have observed as the sub-gap defect states for the deteriorated films. Thus it is reasonable to consider that GeO_2 films have a tendency to become oxygen deficient in N_2 ambient, and that deficiency increases through the generation and volatilization of GeO. Thus the amount of volatilized GeO determines the amount of sub-gap defects in GeO_2 films.

From thermodynamic considerations, it is reasonable to consider that the annealing in O_2 ambient with high pressure reduces the oxygen deficiency in GeO_2. Thus the effects of O_2 pressure (pO_2) in the annealing ambient on k spectra of GeO_2 films were investigated. As shown in **Fig. 5**, the sub-gap photo-absorption dramatically decreases as pO_2 in the annealing ambient increases. This result shows that the density of sub-gap defects strongly correlates with the oxygen deficiency of the film. It is found that the sub-gap defects are generated even by the annealing in oxygen ambient, as long as pO_2 is below ~ 30 atm (at 550°C). The oxygen deficiency in GeO_2 is determined by the temperature and pO_2, as schematically drawn in **Fig. 6**, which explains why high pO_2 is required to grow a high-quality thermal GeO_2 film at higher temperature [6], whereas 1 atm-O_2 is enough to form a relatively good quality film at lower temperatures. In general, the annealing at higher temperature is beneficial to improve the film quality, thus the control of pO_2 at high temperature is inevitably important.

4. Conclusions

The deterioration of GeO_2/Ge stack, through a generation of bulk defects in GeO_2 film, was clearly observed as an increase of sub-gap photo-absorption of the film. It was found that the amount of GeO volatilized from the stack determined the density of the sub-gap defect states. The generation of those defects was suppressed when the film was annealed in high pO_2 ambient since those defects correlate with oxygen deficiency of the films.

Acknowledgements

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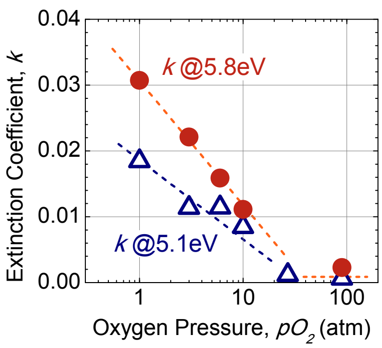

Fig. 5 Values of extinction coefficients (k) at 5.1 eV and 5.8 eV as a function oxygen pressure (pO_2) in the annealing ambient for the films annealed at 550°C (initial thickness: 140 nm). The sub-gap defect generation was clearly detected after lower-pO_2 annealing but completely suppressed after higher-pO_2 (>30atm) annealing.

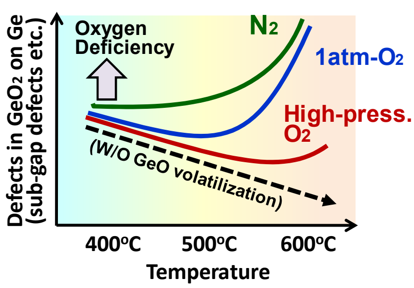

Fig. 6 Schematic of defect density in GeO_2 films annealed in different ambient (N_2, 1-atm O_2, and high-pressure O_2) at various temperatures. At higher temperature, a higher-pO_2 is required to improve the film quality by suppressing the oxygen deficiency, while a lower pO_2 is enough to suppress it at lower temperature. The dotted line represents the improvement of the film quality by a structural relaxation when GeO volatilization is completely suppressed.