Far Infrared Study of Structural Distortion and Transformation of HfO$_2$ by Introducing a Slight Amount of Si

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1. Introduction

Hafnium dioxide is one of the most promising candidates of the substitution for SiO$_2$ as gate dielectrics. However, HfO$_2$ can be easily crystallized during thermal annealing process. To suppress HfO$_2$ crystallization, the incorporation of Si atoms into HfO$_2$ film is one of the efficient solutions. On the other hand, it has not been fully understood how the crystal structure of HfO$_2$ film is changed with the incorporation of Si atoms. To investigate this issue, we used the transmission Fourier transform infrared spectroscopy (FTIR) ¹, because it can clearly detect the HfO$_2$ crystallization and its microscopic bonding state change in far infrared (IR) region.

In this work, we investigated a change of HfO$_2$ structure as functions of Si concentration and annealing temperature. Furthermore, we investigated the crystallization of very thin HfO$_2$ films as a function of film thickness so as to clarify an effect of Si diffusion into HfO$_2$ film on its bonding structure.

2. Experimental

Floating-zone Si wafers were employed for the present study to reduce Si-O absorption in the Si substrate as possible. The Hf$_{1-x}$Si$_x$O$_2$ films were deposited by reactive sputtering (in Ar + O$_2$), and very thin HfO$_2$ films were deposited by RF sputtering (in Ar). The samples were annealed at 400 - 1000 °C in N$_2$ ambient at the atmospheric pressure. We measured the IR absorption in far IR region with transmission FTIR. We also used the glazing incidence x-ray reflectivity (GIXR) to determine the film thicknesses, the x-ray diffraction (XRD) to determine the film crystal structure, and the x-ray photoelectron spectroscopy (XPS) to determine the Si concentration in the film.

3. Result and Discussion

The IR absorption spectra of 20 nm Hf$_{1-x}$Si$_x$O$_2$ film are shown in Fig. 1. All the samples were annealed at 1000 °C in N$_2$ ambient for 5 minutes. The peaks at 260, 325, 400 and 510 cm$^{-1}$ (vertical solid line in Fig. 1) are assigned to the monoclinic HfO$_2$ phonon modes ²,³. Increasing the Si concentration, the absorption of monoclinic HfO$_2$ phonon modes, particularly at 325 cm$^{-1}$, drastically decreases. Furthermore, the spectrum of Hf$_{1-x}$Si$_x$O$_2$ (x~ 0.10) shows a broad peak which is centered at 450 cm$^{-1}$ (vertical dashed line in Fig. 1). The crystal structure of those samples was measured with XRD as shown in Fig. 2. It is clearly seen that the HfO$_2$ film is transformed from the monoclinic to an unidentified structure in our XRD. Nevertheless, it should be assigned to the orthorhombic, the tetragonal or the cubic of HfO$_2$. In any case, the broad peak in Fig. 1 corresponds to the phonon mode of that phase of HfO$_2$, as is the case of ZrO$_2$ ⁴.

From the result of Fig. 1 and Fig. 2, it is found that the Si solubility of monoclinic HfO$_2$ is less than 10 at. %. On the other hand, not only the peak intensity of IR absorption spectra but also the intensity ratio among monoclinic HfO$_2$ absorption peaks drastically changes with Si concentration, though Si incorporation less than 5 at. % keeps the monoclinic phase of HfO$_2$. This fact means that incorporated Si atoms distort the monoclinic HfO$_2$ structure due to the different bonding properties of Si in terms of ionicity or coordination number.

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Though the monoclinic HfO\textsubscript{2-x}Si concentration in the film. The relationship among the mixture of each kinds of structure depending on the amorphous or monoclinic or unidentified crystal structure annealed at 600 and 800 °C show the IR spectrum of becomes small and the structural phase is strongly distorted.

In Fig. 3, the IR absorption spectra of Hf\textsubscript{1-x}Si\textsubscript{O} are shown as a function of annealing temperature. As-deposited samples show a broad peak, which indicates that as-deposited HfO\textsubscript{2} structure is amorphous.\textsuperscript{22} The samples annealed at 600 and 800 °C show the IR spectrum of amorphous or monoclinic or unidentified crystal structure or the mixture of each kinds of structure depending on the Si concentration in the film. The relationship among Hf\textsubscript{1-x}Si\textsubscript{O} structure, annealing temperature and Si concentration is summarized as a phase diagram in Fig. 4. Though the monoclinic HfO\textsubscript{2} phase appears at a high temperature, it should be noted that the crystallized component becomes small and the structural phase is strongly distorted with the increase of Si concentration.

The Si incorporation has a significant effect not only on the Hf\textsubscript{1-x}Si\textsubscript{O} film but also on very thin HfO\textsubscript{2} film, because Si atoms diffuse into HfO\textsubscript{2} film from Si substrate during the thermal annealing process. Then we investigated the IR absorption of very thin HfO\textsubscript{2} films as a function of the film thickness (Fig. 5). As expected, the thinner HfO\textsubscript{2} shows a weaker absorption intensity of monoclinic HfO\textsubscript{2}. However, the peak intensity ratio changes with decreasing the film thickness and 2.4 nm HfO\textsubscript{2} sample shows a broad peak around 450 cm\textsuperscript{-1} beyond an experimental uncertainty. This result is quite similar to that of Fig. 1. Therefore it is supposed that the HfO\textsubscript{2} film thinner than 10 nm contains a few at % Si atoms, and that very thin HfO\textsubscript{2} film (< 2 nm) contain Si atoms which concentration is high enough to transform the film crystal structure. This will affect the dielectric properties of the thin film.

4. Conclusion

We investigated the distortion and transformation of the HfO\textsubscript{2} structure as functions of the amount of incorporated Si and the annealing temperature with FTIR. It is found that the IR absorption spectra of monoclinic HfO\textsubscript{2} drastically change with a slight amount of Si incorporation. On the other hand, the incorporation of Si more than 10 at. % transforms the HfO\textsubscript{2} structure from the monoclinic to an unidentified phase at 1000 °C. This result indicates that the monoclinic HfO\textsubscript{2} structure is distorted with the incorporated Si atoms. Furthermore, it is demonstrated that Si atoms diffused from the Si substrate affect the crystal structure of thin HfO\textsubscript{2} film.

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References