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New structural properties of ferroelectric Y_2O_3-doped HfO_2 films probed by microscopic Raman spectroscopy measurements

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Abstract

The ferroelectricity of Y_2O_3-doped HfO_2 is reported from the structural viewpoints. No monoclinic phase of Y_2O_3-doped HfO_2 is observed in XRD, while significant monoclinic phase contribution to Raman shift is clearly observed for the first time. This fact is discussed from inhomogeneous ferroelectricity in HfO_2-based materials.

1. Introduction

HfO_2 has been used for advanced CMOS gate stacks for these ten years. To further scale down CMOS devices, aggressive EOT reduction is more needed. On the other hand, a new functionality of gate stacks will provide a new way to extend semiconductor device technology. Ferroelectric materials have been considered as a potential candidate for such functional devices. Nevertheless, ferroelectric materials such as PZT, SBT or BST were hard to employ in Si CMOS manufacturing, because conventional ferroelectric materials were obviously contaminants for conventional CMOS devices. Recently it was found that doped HfO_2 showed ferroelectric properties (1, 2). More recently, we reported that even un-doped HfO_2 showed ferroelectric properties by taking care of its interfaces (3). It is obvious that ferroelectric HfO_2 substantially solves above problems of conventional ferroelectric materials, because HfO_2 is now used in the CMOS front-end process. Therefore, 1T (para-HfO_2)-1cap (ferro-HfO_2) type Fe-RAM, for example, as shown in **Fig.1**, will be realized without any material or process penalties. However, it is not clearly understood what structure is responsible for the ferroelectricity and what type of ferroelectricity is realized in HfO_2.

Fig. 1 HfO_2 films can have both paraelectric and ferroelectric properties. In the simplest applications, it will be possible to use HfO_2 both for advanced gate stack and for ferroelectric capacitor using the conventional front-end process.

This paper focuses on structural properties of Y_2O_3-doped HfO_2 (Y-HfO_2) from the comparison of XRD with Raman spectroscopy. Raman spectroscopy results are demonstrated in doped HfO_2 films for the first time.

2. Experimental

It is generally not easy to detect clear signals from thin films in the Raman spectroscopy measurement due to a huge background from the substrate. Therefore, Y-HfO_2 films were prepared on SiO_2 membrane on Si chips, as shown in **Fig. 2**. The SiO_2 membrane thickness was 200 nm (200 μm square). 300-nm-thick Y-HfO_2 was deposited by co-sputtering of HfO_2 and Y_2O_3 targets, followed by annealing at 700°C in N_2. Y-doping was controlled to be 5% to show almost highest ferroelectricity (4), in which % is Y-atomic % of (Y+Hf). XRD was measured by Cu-Kα, and the Raman shift was carried out by He-Cd laser (λ=325 nm) to enhance the surface sensitivity in thin film Raman measurements.

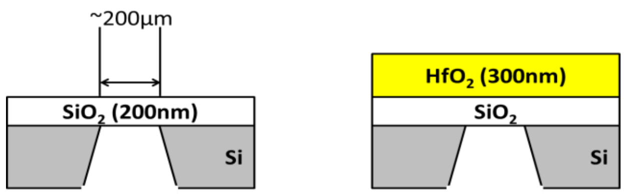

Fig. 2 200-nm-thick SiO_2 membrane formed on Si chip was used. 300-nm-thick HfO_2 and Y-HfO_2 were deposited on SiO_2. Microscopic Raman spectroscopy measurement was carried out from the top through HfO_2 and SiO_2 membrane. Since small Si signals and broad background was overlapped on small HfO_2 signals in case on Si chip, the membrane structure was quite effective for the Raman spectroscopy measurements of thin HfO_2.

3. Results

XRD patterns are shown in **Fig. 3** for both un-doped and Y-HfO_2. The un-doped one shows monoclinic phase dominantly, in addition to a small symmetric phase (cubic, tetragonal or orthorhombic), while Y-HfO_2 shows only the symmetric phase. The same structural change of HfO_2 was reported for achieving higher-k cubic phase HfO_2, but the ferroelectricity was not noticed (5).

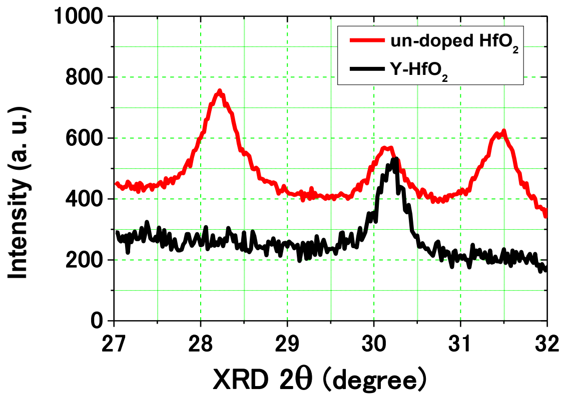

Fig. 3 XRD patterns of both un-doped HfO_2 and 5% Y-HfO_2. By introducing only 5% Y_2O_3 to HfO_2, no monoclinic XRD pattern is observed. Both films were annealed at 700°C in N_2.

Next, the Raman spectroscopy results of both samples are discussed. **Fig. 4** shows the Raman shifts of un-doped HfO_2, Y-HfO_2, and membrane SiO_2. When the Raman shifts of the un-doped HfO_2 film is compared with that of experimentally obtained and theoretically calculated Raman peaks in the literatures (7, 8), the monoclinic peaks are well reproduced. On the contrary, though several peaks around 250 cm^{-1}, 390 cm^{-1}, 550 cm^{-1}, and 640 cm^{-1} disappear in Y-HfO_2, it is noted that the Raman shift peaks of Y-HfO_2 sample are not in agreement with results obtained theoretically and experimentally for non-monoclinic HfO_2, and most of peaks are on the monoclinic peak positions.

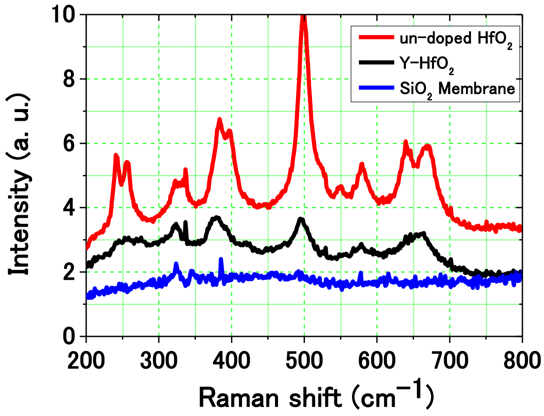

Fig. 4 Raman spectroscopy results both for un-doped HfO_2, Y-HfO_2 and SiO_2 membrane only. Several peaks observed in un-doped HfO_2 disappear in Y-HfO_2. Nevertheless, major monoclinic peaks observed in un-doped HfO_2 still remains in doped case. Note that the SiO_2 membrane background is kept low enough.

4. Discussion

Raman shift results characterize the local bonding vibration mode, while XRD shows the long-range ordering. So, it means that many monoclinic Hf-O bonding still remains locally in Y-HfO_2, though XRD does not show the crystalline structure. In fact, it was reported that the ferroelectricity was observed in doped HfO_2 though no orthorhombic phase was observed in XRD (9). Therefore, it is not appropriate to conclude the origin of ferroelectricity in doped HfO_2 simply from XRD results. Furthermore, the fact that the "wake-up" effect is observed (9, 10) may imply that the ferroelectric embryo rather than the nucleation may be distributed in the film, as schematically shown in **Fig. 5**. We have also observed the "wake-up effect" in this Y-HfO_2 (data not shown). It is suggested that the present ferroelectricity is not homogeneous. Thus, to improve ferroelectricity of HfO_2, it will be important to help the nucleation not only by doping but also by controlling its interfaces (3).

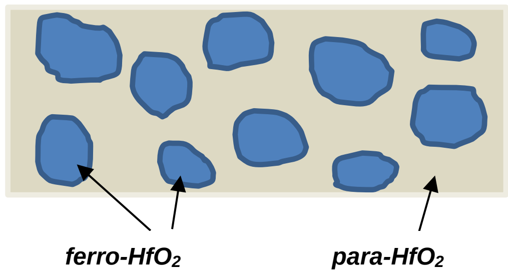

Fig. 5 Schematic image of Y-HfO_2. It shows the coexistence of monoclinic and other symmetric phases. Note that no monoclinic HfO_2 is detected in XRD as shown in Fig. 3. This implies that a large amount of Y-HfO_2 is composed of the embryo state for the ferroelectric phase with monoclinic Hf-O bonding characteristics, while a small part is nucleated to the ferroelectric phase.

Conclusion

Ferroelectric doped HfO_2 films were studied by Raman spectroscopy measurements for the first time. Our results suggest that ferroelectric doped HfO_2 is not with homogeneous phase but mixed one. Although it is not clear so far whether this is intrinsic or not, we cannot conclude that XRD result is the direct evidence for a single phase of ferroelectric film formation of HfO_2. Not only doping into HfO_2 but also interface control at HfO_2 will become substantially more important.

Acknowledgement

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