Structural Investigation of Epitaxial HfO_2 Films by X-ray Scattering

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Introduction

High-k material HfO_2 is a potential candidate for replacing SiO_2 as a gate dielectric in metal oxide-semiconductor (MOS) devices. Amorphous HfO_2 has been profoundly studied but may not be adequate due to the low re-crystallization temperatures.[1] A high electrical leakage occurs at grain boundaries, which are formed when amorphous films turn into polycrystalline. Epitaxial single-crystal oxide thin films and their interfaces with semiconductors are generally more robust during the high temperatures annealing. Therefore, the growth of high quality epitaxial HfO_2 films is pursuited and may provide advantages as the gate dielectric.[2]

Methods and Materials

Nano-thick HfO_2 epitaxial thin films have been grown on GaAs (001) substrates by molecular beam epitaxy with a two-step method. The initial deposition of HfO_2 was performed at room temperature and an amorphous layer was formed. In-situ annealing to ~530°C lead to the formation of an epitaxial single crystal HfO_2 layer, which serves as a template for the subsequent epitaxial over-growth of HfO_2 at higher temperatures. Synchrotron X-ray scattering and reflectivity were employed to characterize the structural properties of these films.

Results and Discussion

The intensity profile of a θ-2θ scan along surface normal of a sample with a ~ 9 nm thick HfO_2 layer is illustrated in Fig. 1. The abscissa is in units of GaAs reciprocal lattice units (r.l.u.$_{GaAs}$). The X-ray reflectivity curve, the part of L ≤ 1 r.l.u.$_{GaAs}$, can be well fitted by a single-layer model consisting of a 9.1 nm thick HfO_2 layer without interfacial layer. The periodic oscillations persist up to 8 nm^{-1} indicating the presence of an atomically sharp interface, which is further confirmed by cross sectional transimission elelctron microscope images. In addition to the sharp (0 0 2) Bragg reflections of GaAs substrate, the broad peaks on the high L side is indexed as the (0 0 2) reflection of monoclinic phase HfO_2 (m-HfO_2). On the low L size, another broad peak, whose intensity is more than two orders of magnitude weaker than that of HfO_2 (002) is attributed to the (-1 1 1) reflection of m-HfO_2. The intensity ratio of (0 0 2) to (-1 1 1) reflections increases with deccreasing film thickness indicating that the film is predominantly consistant of (0 0 1) oriented m-HfO_2 together with a (-1 1 1) oriented minority, especially in the case of ultra-thin films.

Careful analysis of the epitaxial relatioship between the (0 0 1) oriented HfO_2 layer and substrate was carried out using four-circle x-ray diffraction. A broad peak centered at ~2.2 r.l.u.$_{GaAs}$ was observed at the radial scan across GaAs (0 2 0) surface reflection, which confirms the alignment of in-plane axes. If the m-HfO_2 films were perfect single crystals, the ϕ scans across the HfO_2 (0 4 0) and (4 0 0) reflections would have a characteristic two-fold and one-fold symmetry, respectively. The observed four-fold rotational symmetry in both ϕ scans shown in Fig. 2a strongly suggest that the (0 0 1)-oriented HfO_2 films consist of four subdomains which rotate 90° with respect to each other. Fig. 2b shows an H-L mesh scan near the HfO_2 (4 0 0) reflection with the axes displayed in the r.l.u. of m-HfO_2. The lobe on the top is the (4 0 0) reflection of one domain and the lobe on the bottom, centered at (4 0 -0.572)$_{HfO2}$, matches perfectly the location of the (0 4 0) reflection of another m-HfO_2 frame whose in-plane rectangular lattice net is rotated 90° from the former one.

In summary, high quality m-HfO_2 epitaxial films have been grown on GaAs (0 0 1). The films are predominantly (0 0 1) oriented with the coexistence of four domains of 90° in-plane rotation with respect to each other.

References

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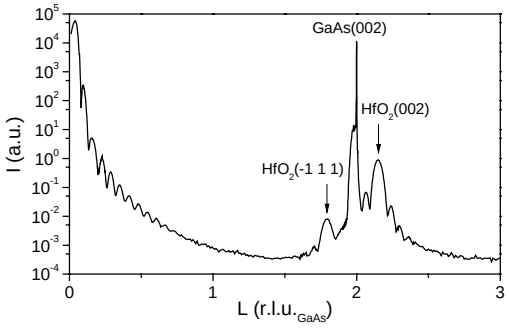

Fig. 1. θ-2θ scan along surface normal.

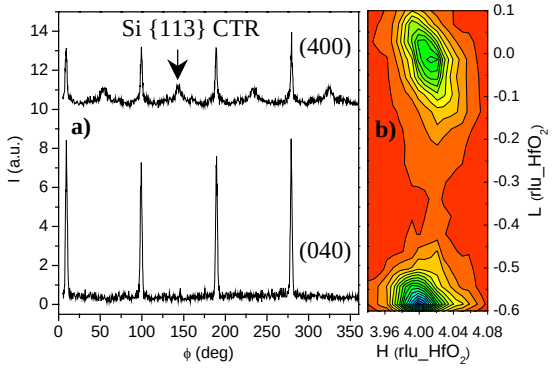

Fig. 2. a) ϕ scans across m-HfO_2 {400} and {040} reflections. b) a K-L mesh scan near m-HfO_2 (400) surface reflection.