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Epitaxial anatase HfO_2 on high-mobility substrate for ultra-scaled CMOS devices

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ABSTRACT

On the basis of ab initio simulations, the formation of an epitaxial phase that has the anatase structure has been proposed as the microscopic mechanism responsible for the preferential orientation of monoclinic HfO_2 films on the high-mobility (0 0 1) oriented Ge and GaAs substrates. In fact, the oriented monoclinic structure follows the in-plane axis of the anatase phase as proved by X-ray scattering measurements. The fact that epitaxial HfO_2 anatase has no bulk counterpart is explained by our calculations as due to the unfavorable Helmholtz free energy of anatase phase when the condition of epitaxy is released.

Since its formulation in 1965, Moore's law—stating that the number of transistors that can be inexpensively placed on an integrated circuit is increasing exponentially, doubling approximately every two years—has described an important trend in the history of computer hardware for more than four decades [1]. Presently, the continuous scaling down of complementary metal oxide semiconductor (CMOS) devices to smaller and smaller size is facing the problem of replacing the SiO_2 film that has been used by microelectronic industry as gate oxide up to the present generation of CMOS transistors. In fact, when the oxide thickness is of the order of few nanometers, the electrons can tunnel through the SiO_2 producing a leakage current that prevents the device to work. To identify an ideal candidate to substitute SiO_2, both experimental and theoretical efforts were focused on oxides that present high dielectric constant (κ), the so-called high-κ oxides. Among them, hafnium dioxide, HfO_2, has recently attracted considerable interest due to the high-κ (baddeleyite HfO_2 has $\kappa = 16$, considerably higher than the dielectric constant of SiO_2, $\kappa = 3.9$ [2]), and the appropriate conduction band off-set with the Si substrate (experimental values are in the 1.5–2.0 eV range [3]). Due to the replacing of SiO_2 with alternative oxides, Si has lost its leadership as preferred substrate, and semiconductors that have a higher electron mobility than Si, such as Ge or GaAs, have been investigated to replace Si in the next generation of ultra-scaled CMOS.

Due to the large mismatch (~8%) between the oxide and the semiconductor, the unexpected preferential orientation of monoclinic (baddeleyite structure) hafnium di-oxides on Ge [4] and GaAs [2,5] (0 0 1) high-mobility substrates has puzzled, in the past years, material scientists interested in a defect-free interface for nano-electronic applications.

The preferential orientation of baddeleyite HfO_2 on (0 0 1) oriented Ge and GaAs substrates is analyzed by X-ray diffraction (Fig. 1) on HfO_2 layers grown by atomic layer deposition at 375 °C, using $HfCl_4$ and H_2O as precursors [5]. The comparison of the data of top and bottom panel of Fig. 1 provides clear experimental evidence that monoclinic HfO_2 (m-HfO_2) has the same

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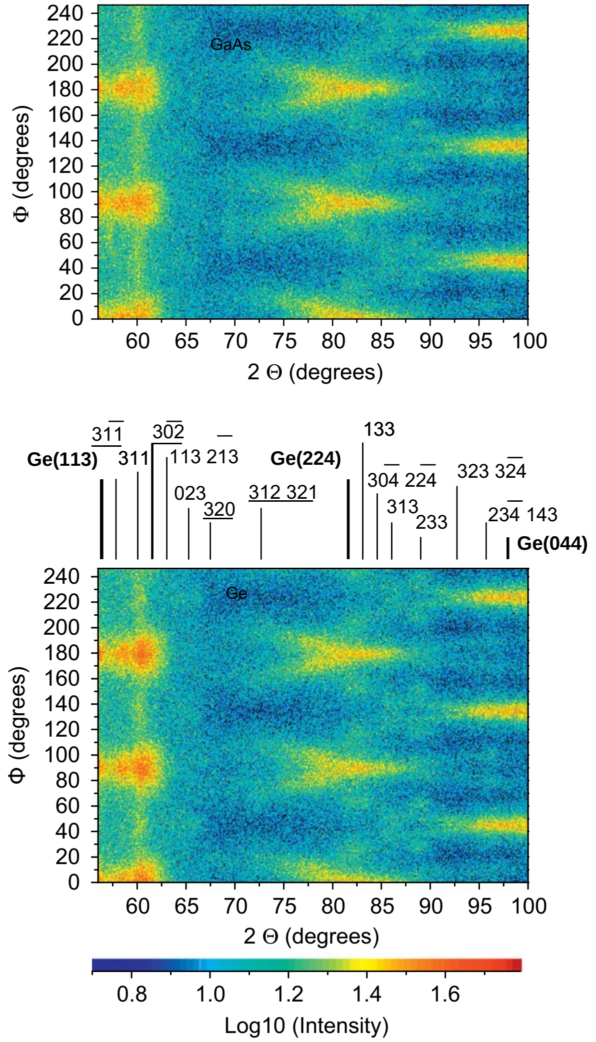

Fig. 1. (Color online) ϕ maps acquired at grazing incidence (1°) configuration showing the same preferential orientation of baddeleyite HfO_2 on Ge (bottom panel) and GaAs (top panel) (0 0 1) oriented substrates. The HfO_2 thickness is 8.8 nm on GaAs and 9.6 nm on Ge.

orientation on the two substrates, with m-HfO_2(0 0 1)// Sub(0 0 1), m-HfO_2(0 1 0)//Sub(0 1 0) (where Sub = Ge, GaAs). From complementary X-ray diffraction analysis (not shown), the in-plane lattice parameters of oriented m-HfO_2 film are equal to $a_m = b_m = 5.43$ A, and they have the same value for both Ge and GaAs substrates.

The lattice parameter of Ge, $a_{Ge} = 5.657$ A, [6] differs only by ~0.05% from the GaAs one, $a_{GaAs} = 5.654$ A [6]. Monoclinic hafnium dioxide film presents the same preferential orientation on GaAs and Ge, i.e., two substrates having different electronic composition but same lattice parameter. On the contrary, there is no experimental evidence of any preferential orientation on Si (0 0 1) substrate (Si has the same number of valence electrons than Ge but a lattice parameter ~4% smaller); attempts of growing HfO_2 on Si (0 0 1) substrate has produced only random orientation [7]. These facts suggest that the lattice parameter of the substrate rather than the electronic composition may play an important role in determining the oriented growth of HfO_2.

In a recent publication [8], on the basis of first principle calculations, we have proposed that the microscopic mechanism responsible for the oriented growth of HfO_2 on Ge and GaAs (0 0 1) surfaces is due to the formation of HfO_2 epitaxial film with tetragonal symmetry and with the structure of the anatase, structurally stabilized by the requirement of matching the lattice parameter of the substrate (i.e. by the epitaxy condition). According to our calculations [8], the observed preferential orientation of the monoclinic structure is related to the relaxation of the epitaxially stabilized anatase phase when the oxide film reaches a critical thickness, which for Ge (0 0 1) substrate is of the order of 10 nm. In fact, as can be noticed from Fig. 1, the preferential orientation of the monoclinic structure follows the in-plane axis of the anatase phase, as proven by accurate X-ray scattering measurements [8]. The predicted anatase phase has a dielectric constant of $\kappa \sim 11$ [8], i.e., comparable to the bulk monoclinic one, and is almost lattice matched with the Ge (or GaAs) substrate, allowing to control at the atomic level, its interface with the semiconductor producing—at least in principle—a defect free interface, as it is required for the integration of high-κ dielectrics in future CMOS devices.

However, at the best of our knowledge, the anatase structure is not one of the HfO_2 bulk polytypes experimentally detected, in contrast with TiO_2 [6], a similar oxide where anatase is commonly observed (Ti and Hf are in the same column of the periodic table). To understand the reason why the anatase is not known as a bulk phase of HfO_2 we have investigated the relative stability of different HfO_2 phases by computing the Helmholtz free energy of the crystal structures as a function of temperature, that reads:

$$F = U^{eq} + k_B T \sum_i \ln\left[2\sinh\left(\frac{\hbar\omega_i}{2k_B T}\right)\right] \tag{1}$$

where U^{eq} denotes the electronic energy with atoms placed at their equilibrium position, k_B is the Boltzmann constant, ω's are phonon frequencies that we have computed with harmonic approximation since the temperature range of interest (i.e., up to 1200–1500 K, the melting temperature of the substrate) is well below the melting temperature of HfO_2 and we do not expect, in our case, anharmonic effects to play any important role. The calculation of the present work is performed by plane-wave pseudopotential techniques in a similar way as done in Refs. [8,9]; interested readers can refer to these papers for the computational details.

Three low-pressure polymorphs of HfO_2 are known: a cubic phase having the fluorite structure, a tetragonal phase having the distorted fluorite (DF) structure, and a monoclinic phase having the baddeleyite structure. At low temperature [10], the cubic phase of HfO_2 (fluorite) is structurally unstable due to the presence of soft phonon modes at X-point of the Brillouin zone that drives the system into a tetragonal phase that has the DF crystal structure [9]. The resulting DF structure for bulk crystal is displayed in the left panel of Fig. 2. As suggested in Ref. [9] on the basis of first principle simulations, the cubic phase