

## Supplementary Information

### Nanoscale continuous transition from monoclinic to ferroelectric orthorhombic inside HfO<sub>2</sub> nanocrystals stabilized by HfO<sub>2</sub> capping and self-controlled Ge doping

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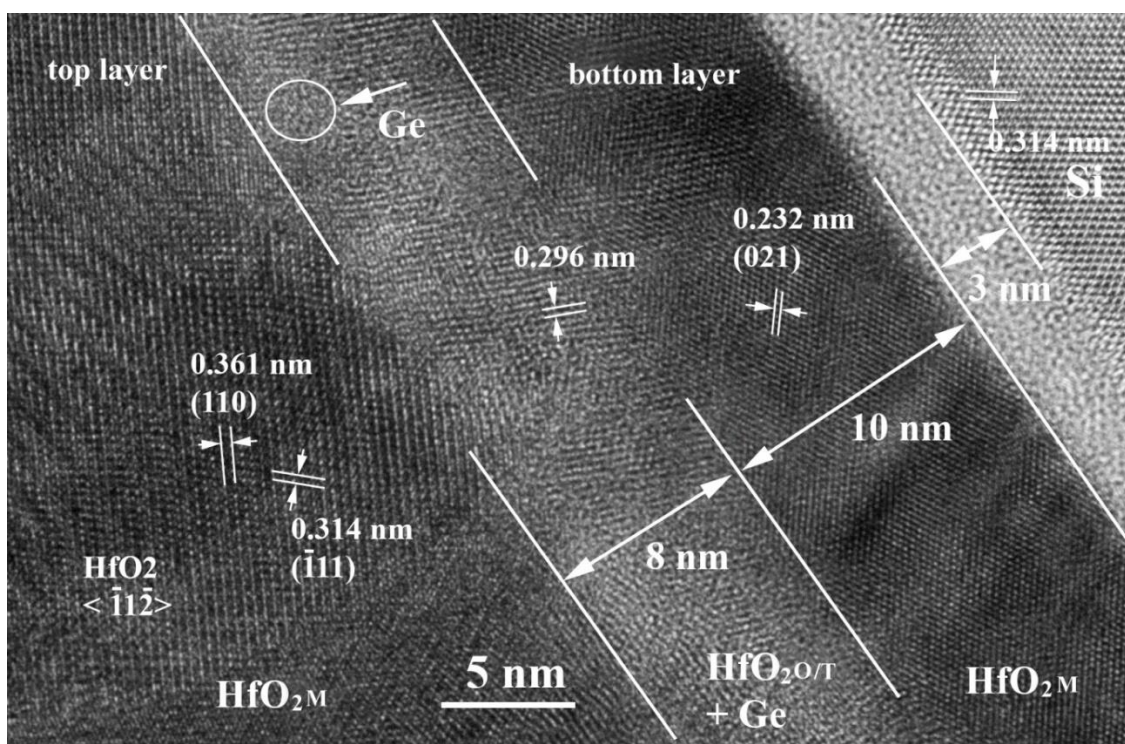
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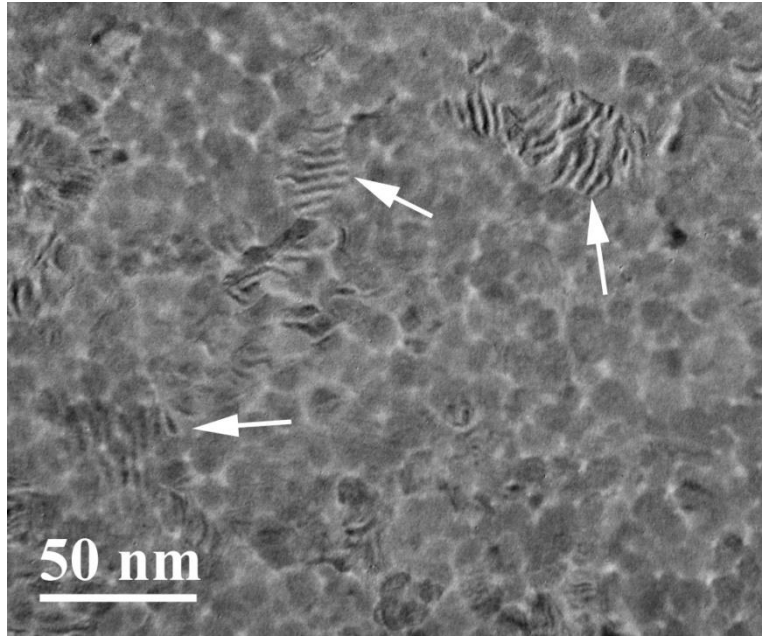
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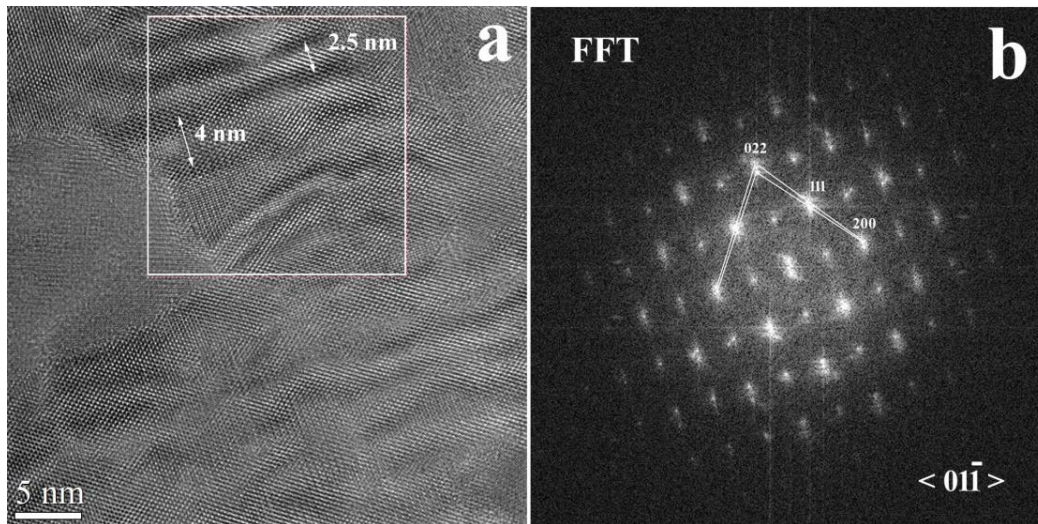
#### Supplementary TEM images



**Figure S1.** High resolution XTEM image of the S4 sample. In the intermediate layer ( HfO<sub>2</sub> +Ge) there are small nanocrystallites of orthorhombic HfO<sub>2</sub> phase and amorphous germanium nanoparticles Ge-NP (encircled).



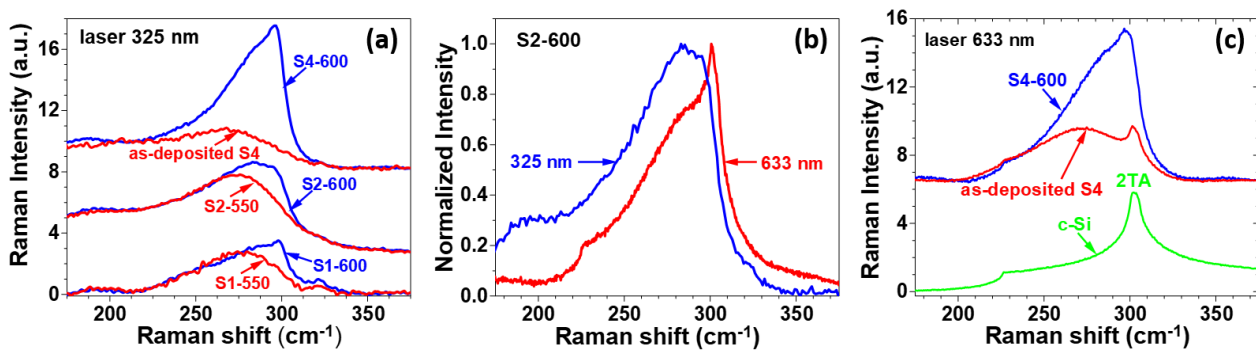
**Figure S2** Low magnification plan view image showing the moiré fringes formation.



**Figure S3.** HRTEM image of the plan view S3-600 sample (a) and the corresponding FFT pattern (b). The (200), (111) and the (022) are splitted in the FFT pattern, formed by the superposition of the similar spots of the T, O and deformed M phases. The source of the moiré fringes can be associated with the splitting of the  $\{111\}$  type spots due to the phase transformation from the tetragonal to orthorhombic or monoclinic phases.

**Raman scattering analysis.** Therefore, the Ge-Ge vibration mode was clearly detected in the investigated 3-layer samples by  $\mu$ -Raman scattering using UV excitation laser emitting at 325 nm (Figure S4a), even if Ge NCs are not evidenced by XRD measurements (Figure 10a). Instead, the

presence of multiple peaks specific to  $\text{HfO}_2$  crystallites is not detected within  $\mu$ -Raman spectra of our samples.



**Figure S4.** Ge-Ge vibration peak in  $\mu$ -Raman spectra of 3-layer Ge- $\text{HfO}_2$  samples: (a) annealing increased crystalline ordering in Ge NPs; (b) comparison of the  $\mu$ -Raman spectrum measured by 325 nm and 633 nm laser excitation on S2-600; (c) comparison of spectra measured on S4-600 and as-deposited S4, and spectrum measured on c-Si substrate, for 633 nm laser excitation light. (see Table 1 of the main text for sample labels).

The spectra show the blue shift and increase of Raman peak intensity by RTA at 600 °C corresponding to the increase of size, number or/and of the crystalline ordering in Ge NPs (Figure S4a). This effect is more pronounced in sample S2 with the Ge- $\text{HfO}_2$  intermediate layer thickness  $d_{\text{int}}$  of about 20 nm than in S1 with  $d_{\text{int}} \sim 10$  nm (Table 1). The formation of Ge NCs (NPs) by RTA at 600 °C is more significantly enhanced in the 3-layer structure S4 in comparison to the as-deposited S4 sample by reducing the thickness of  $\text{HfO}_2$  control layer  $d_{\text{ctr}}$  from  $\sim 60$  nm (S1, S2) to 30 nm. The less constrain induced by a thinner control layer gives more freedom for Ge segregation and NPs/NCs formation from the Ge- $\text{HfO}_2$  intermediate layer underneath.

The use of UV light of 325 nm wavelength has the advantage of a stronger absorption in the Ge containing layer and thus to less penetrate in c-Si substrate lowering its contribution to the weak Ge-Ge peak as in the case of using a laser emitting at longer wavelength. The Raman spectra measured on sample S2-600 using 325 and 633 nm excitations are compared in Figure S4b. The spectrum measured with 633 nm excitation presents the 2TA mode of Si substrate ( $\sim 301 \text{ cm}^{-1}$ ) and a shoulder positioned around  $286 \text{ cm}^{-1}$ , while the 325 nm spectrum has a broad maximum positioned at  $\sim 286 \text{ cm}^{-1}$ . The  $286 \text{ cm}^{-1}$  features are clearly due to Ge-Ge bonds and reflect the formation of Ge clusters at the start of Ge nanocrystallization, better revealed by the 325 nm

spectrum. The contribution of the Raman scattering in c-Si substrate is clearly evidenced in Figure S4c by the comparison of the Raman spectra measured on samples S4 using 633 nm laser and that measured on bare Si substrate. The spectrum of as-deposited S4 sample shows a broad maximum centered at  $\sim 271 \text{ cm}^{-1}$  typical for amorphous Ge and a sharp peak at  $\sim 303 \text{ cm}^{-1}$  corresponding to the second order mode in the Si substrate (2TA mode)<sup>5</sup>. By annealing, the maximum corresponding to Ge-Ge optical phonon mode sharpens and its intensity increases, and also its position changes to  $\sim 298 \text{ cm}^{-1}$ , meaning that Ge NCs are formed in the S4-600 sample.