Supporting Information

Origin of Indium diffusion in high-*k* oxide HfO_2

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Details on substitutional In_{Hf} diffusion

Based on the formation energy analysis, we found that the most energetically favorable In substitutional point In_{Hf} dominates during the large range of oxygen chemical potentials. However, the high stability of the point defect might not be feasible to diffuse. In the following, we calculate the diffusion of this specific defect. In this diffusion process, the snapshots of initial, transition, and final states are displayed. The energy barrier is as high as 7.36 eV, with the saddle point corresponding to an exchange angle of 39.4° (exchange angle is defined as the angle between the In-Hf dimer and its original counterpart). The exchange angle deviates from 90° since the exchange path is not symmetric due to a V_O presence along the In_{Hf} diffusion path while absence along the Hf diffusion path.

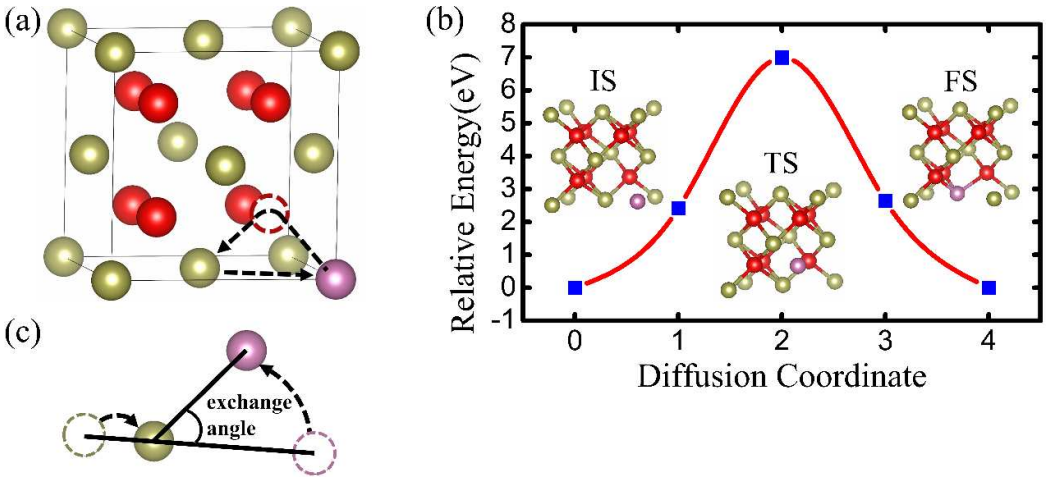

Figure S1. (a) Schematic diagrams of In diffusion pathways between two adjacent substitutional Hf-sites, (b) its energy barrier curve. Three snapshots representing the initial (IS), transition (TS), and final state (FS), are also included and (c) schematic diagram of exchange angle of the exchange process between In_{Hf} and a Hf.

Dependence of relative energy of supercell with $In_{O,T}$ on lattice constants

It is noted that In point defect along with oxygen vacancy ($In_{I,O}$+V_O) has a relatively higher formation energy. In fact, the interfacial strain on HfO_2 would be inevitably introduced during the HfO_2/III-V interface growth process, due to the large lattice mismatch between them (HfO_2: 5.11 Å, GaAs: 5.43 Å).[1,2] To minic growth condition, we calculated the relative energy of supercell with $In_{I,O}$ in the presence of a V_O as a function of the lattice constant variation, as shown in **Figure S2**. It is found that the total energy of the system with 2% tension strain is reduced by ~3.0 eV compared with the pristine lattice constant. In the inset of **Figure S2**, the E_{form} decreases greatly under 2% tension, which practically promotes the feasibility of In interstitial diffusion mechanism facilitated by V_O.

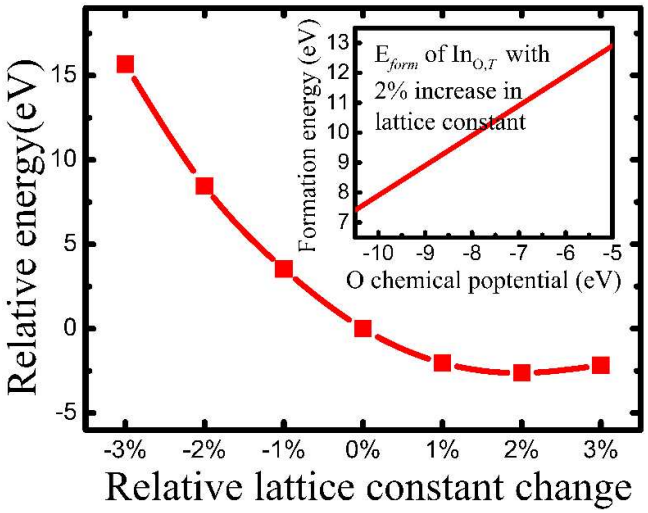

Figure S2. Changes of relative energy of $In_{O,T}$ with lattice constant of HfO_2, where the reference energy is the total energy of supercell with pristine lattice constant. Changes of E_{form} of $In_{O,T}$ with O chemical potential when the lattice constant increases by 2% are also included.

References

[1] KC S.; Dong H.; Longo R. C.; Wang W.; Xiong K.; Wallace R. M.; Cho K. Electronic Properties of InP(001)/HfO_2(001) Interface: Band Offsets and Oxygen Dependence. *J. Appl. Phys.* **2014**, 115, 023703.

[2] Yang Z. K.; Lee W. C.; Lee Y. J.; Chang P.; Huang M. L.; Hong M.; Hsu C.-H.; Kwo J. Cubic HfO_2 Doped with Y_2O_3 Epitaxial Films on GaAs (001) of Enhanced Dielectric Constant. *Appl. Phys. Lett.* **2007**, 90, 152908.