

Strong Dependence of Oxide Work Functions on Surface Structures

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Using density functional theory calculations, we find that work functions of oxides, even for the same surface orientations, strongly depend on both composition and geometry of the surfaces. Oxide surfaces often change their compositions and/or geometric structures depending on the environmental conditions in which they are exposed or prepared, and those deviations might cause significant difference in electronic properties. From atomic-level investigations on various reconstructed surfaces of SrTiO₃ (001), BaTiO₃ (001), TiO₂ (110) and LaFeO₃ (010), we have observed that work functions can be changed up to 5 eV when a surface undergoes compositionally different reconstruction. Moreover, we have observed that, with some stoichiometrically identical surfaces, geometric change can alter the work functions significantly. This work function change can be interpreted partially with surface states, and more importantly, with the potential depth of bulk region modified by surface dipole layer. Our finding reflects the importance of the surface structure on the electron transfer phenomena at oxide surfaces.