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Electronic and Optical Properties of Polycrystalline Metal-oxide Materials

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Although polycrystalline metal-oxide materials and nanopowders are ubiquitous in nature, and find numerous technological applications, surprisingly little is known about their electronic properties. Here, we present recent results on the electronic properties of metal-oxide interfaces and surfaces that have been obtained by quantum-mechanical calculations. These include studies of optical excitation and charge trapping in MgO nanopowders [1], and defect segregation and electron trapping at grain boundaries in MgO and HfO_2 [2-6].

To study the properties of polycrystalline metal-oxide materials we use a hierarchy of theoretical methods including classical shell models, periodic density functional theory and embedded cluster methods (e.g. see ref. 3). The latter is particularly suited to modeling complex polycrystalline systems, and with the use of hybrid density functionals ensures electronic properties can be determined accurately.

Fig. 1 illustrates the application of the embedded cluster approach to modeling the optical properties of MgO nanopowders. Using time dependent density functional theory, we show that Mg and O terminated corners contribute an absorption band centered at about 4.6 eV. We also show that interfaces between nanocrystalites contribute to absorption between 4.5-5.0 eV in good agreement with experiments [1].

Fig. 2 shows how electrons can be trapped by a pristine tilt grain boundary in MgO. This trapping is unusual as the electron is confined inside the dislocation pipe rather that at low-coordinated ions at the interface [2-5]. This effect seems to be quite general as electron trapping by dislocations in MgO has recently been confirmed by measurements made at the Fritz-Haber-Institut. Work is underway to directly confirm the predictions for the (310) boundary by the group of Ikuhara (Univ. Tokyo).

Fig. 3 depicts a diffusion path for a charged oxygen vacancy towards a grain boundary in m-HfO_2. Polycrystalline HfO_2 is used as dielectric layer in metal oxide field effect transistors. These results indicate that segregation of vacancies towards the boundary is favourable and that electron tunneling through defects may dominate leakage current pathways [5,6].

These results have wide-ranging implications for technological applications such as solid oxide fuel cells, catalysts and electronics which will be discussed.

References

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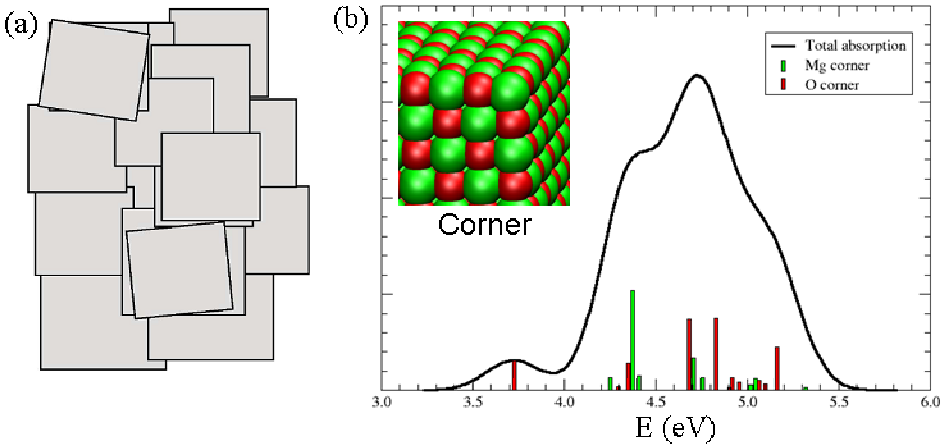

FIG. 1. (a) Typical structure of MgO nanopowder as revealed by transmission electron microscopy. (b) The calculated optical absorption due to Mg and O terminated corners of MgO nanoparticles.

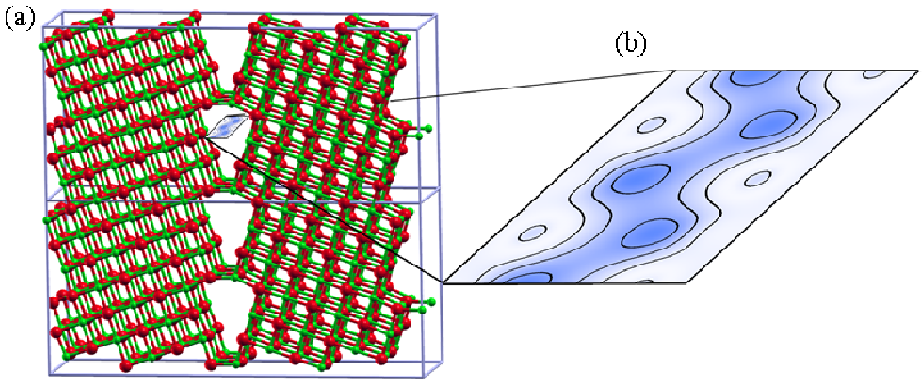

FIG. 2. (a) The calculated structure of the pristine MgO (310)[001] tilt grain boundary. (b) Electron density contour plot showing show electrons are trapped inside the dislocation pipe.

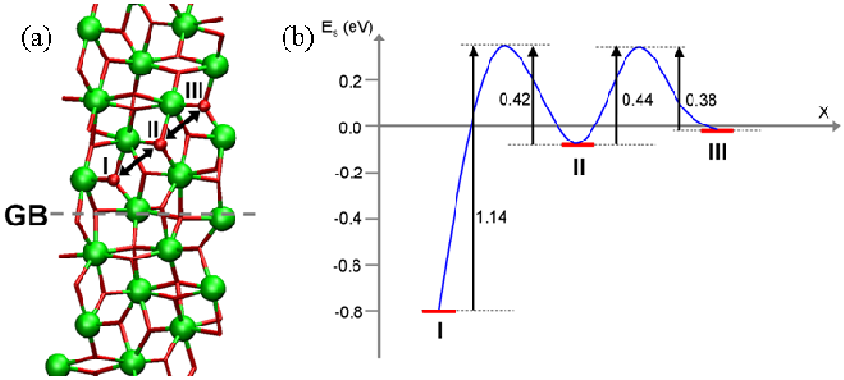

FIG. 3. (a) Lowest activation energy diffusion path for a positively charged oxygen vacancy towards a grain boundary in m-HfO_2. (b) Potential energy surface for diffusion showing strong defect segregation at the grain boundary.