First-principles simulations of MgO tilt grain boundary: Structure and vacancy formation at high pressure

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ABSTRACT

Three $\{n10\}/[001]$ tilt grain boundaries ($n = 2$, 3, and 4) of MgO were studied as a function of pressure from first principles within density functional theory. Our results show that the physical properties of the grain boundary are very distinct from the bulk properties. The predicted symmetric boundary containing well-defined dislocation pipes at zero pressure transforms to asymmetric boundaries with denser structures at higher pressures. The asymmetric boundary structure stable at 50 GPa can be associated with a shear in the boundary plane, whereas the asymmetric boundary structure stable at 100 GPa can be associated with an additional shear in the direction perpendicular to the boundary plane. Unlike in the bulk, several nonequivalent sites exist for vacancy formation in the boundary regions, and the calculated Schottky defect formation enthalpy varies among different boundaries with the $\{310\}$ and $\{410\}$ boundary values at zero pressure being similar to the bulk value. Pressure increasingly stabilizes the boundary vacancies relative to the bulk thereby causing an enhancement in the vacancy concentration, which is further enhanced due to high-binding energy for cation-anion vacancy pairs in the interfacial regions. Also, the grain boundary was shown to induce electronic states in the band gap below the conduction band, which can trap the electrons inside the free space at the interface. Additional states with strong electron localization character appear at the boundary in the presence of the vacancies. Our results are expected to be useful to understand how grain boundaries can serve as primary storage sites for defects and high-diffusion pathways.

Keywords: Grain boundaries, structure, point defects, diffusion, first-principles calculations