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Structures and Energetics of Interfaces in Materials – Ab-initio Local-Density-Functional Theory –

Christian Elsässer

Max-Planck-Institut für Metallforschung, Seestrasse 92, D-70174 Stuttgart, Germany.

Ab-initio density-functional theory of computational condensed-matter physics provides microscopic insights into structural and functional properties of real materials with high accuracy and predictive power. Topic of this contribution is the ab-inito mixed-basis pseudopotential approach [1] for fundamental theoretical investigations of energetic stabilities and microscopic structures of internal boundaries in crystalline materials. The method is based on the density functional theory of inhomogeneous electron gases, with exchange and correlation treated in the local-density approximation (LDFT) [2]. Interfaces and other structural defects of crystals are modelled by means of supercells with periodic boundary conditions. The interactions of atomic nuclei and closed-shell core electrons with electrons in valence and conduction bands are described by norm-conserving pseudopotentials. The valence-band and conduction-band one-electron states are represented by a mixed basis of plane waves and localised functions.

With this theoretical approach, microscopic quantities are accessible for comparison, interpretation and augmentation of experimental observations by transmission electron microscopy (TEM). The formalism yields total energies and atomic forces for structure optimisations, for a quantitative comparison with experimental high-resolution images by TEM, as well as energies and wavefunctions of one-electron states, for an interpretation of experimental electron excitation spectra in TEM. Concerning the latter, calculated site- and angular-momentum-projected local densities of conduction-band states were found useful for a site-specific analysis of experimental energy-loss near-edge structures (ELNES) in core-electron ionisation-edge [3,4]. The capabilities of the approach will be illustrated by selected results from two representative case studies of grain boundaries in ceramics and of metal/ceramic contacts, respectively.

For α-Al_2O_3 as a paradigm ceramic material, four symmetrical tilt grain boundaries were studied: basal $\Sigma 3$ (0001) [5] and prismatic $\Sigma 3$ $(10\bar{1}0)$ [6] twins, rhombohedral $\Sigma 7(\bar{1}012)$ [7] and pyramidal $\Sigma 13(10\bar{1}4)$ [8] twins. The investigated properties are geometric translation states and local atom arrangements, adhesion energetics and electronic structures. The theoretical results are related to experimental TEM observations for the same twin interfaces in bicrystals of α-Al_2O_3 produced by diffusion bonding in ultra-high vacuum [9]. For the rhombohedral $\Sigma 7(\bar{1}012)$ twin, the preferred microscopic interface structure was obtained consistently from LDFT, HRTEM and ELNES [7,9], validating the synergistic approach of ab-initio theory and experimental TEM imaging and spectroscopy. In the latter, the achieved spatial and energetical resolutions were approximately 2 nm and 1 eV, respectively. For the prismatic $\Sigma 3$ $(10\bar{1}0)$ twin, the LDFT calculations yielded two competing interface-stucture variants [6]. For the discrimintation of these by experimental ELNES, it is predicted [6] that a spatial resolution of about 0.2 nm will be required, recommending this twin interface as a promising benchmark case for atom-column-resolution spectroscopy in TEM.

The adhesion energetics, atomistic and electronic structures of thin Pd and Mo films on $SrTiO_3$ (001) substrates were studied [11-13]. Both Pd and Mo are preferably bound on top of O on the substrate surface terminated by a TiO_2 layer. Non-reactive Pd films tend to form atomically abrupt interfaces [11,12]. For Mo, because of its high O affinity, theoretical evidence was found for an energetic instability of the pure film towards the formation of an interfacial oxide reaction layer [13]. The microscopic origins for the different behaviours were analysed in terms of real-space bonding electron densities, local densities of states, orbital bond orders and bond strengths. Experimental TEM results of interfacial O-K ELNES [14] for the same metal/ceramic contacts produced by molecular beam epitaxy [15] are used for comparison and discussion of the theoretical findings.

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