Electron Affinities and Band Offsets of Semiconductors and Insulators, and their use in Electronic Devices

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It is now possible to calculate the band edge energies (electron affinities (EA) and ionization potentials) of semiconductors and insulators using density functional theory. It is well known that density functional theory under-estimates the band gap of semiconductors, which can be corrected using hybrid functionals [1]. However, we must also correct the EAs and IPs [2]. In devices, it is band offsets at semiconductor heterojunctions rather than individual EAs that are usually more important. There are two limiting models of how band offsets relate to EAs, either the electron affinity rule or the matching of charge neutrality levels (CNLs) [3,4]. Although conceptually very different, in practice it is often difficult to distinguish which is correct due to the need for lattice matching or due to similar chemical trends [4]. A clear test case has been found, the heterojuntions (HJ) between two 2D transition metal dichalcogenides; the stacked HJ follows the EA rule, the lateral (in-plane) HJ follows the CNL rule [5]. Photoemission confirms this for the stacked HJ. Various examples of the uses of EAs and band offsets are then given; (a) the choice of HfO2 as the high K dielectric in CMOS [4]; (b) the concept of doping limits in semiconductors and particularly in oxide semiconductors [6], (c) hydrogen pinning levels [7], (d) choice of semiconductors for photo-induced water-splitting [8], (e) choice of electrode materials for OLEDs [9], (f) the use of dipole layers for voltage shifting in CMOS devices [10,11] or dipole layers on quantum dots in photo-luminescent films for HDTV.

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