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Calculated natural band offsets of all II–VI and III–V semiconductors: Chemical trends and the role of cation *d* orbitals

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Using first-principles all-electron band structure method, we have systematically calculated the natural band offsets DE_v between all II–VI and separately between III–V semiconductor compounds. Fundamental regularities are uncovered: for common-cation systems DE_v decreases when the cation atomic number increases, while for common-anion systems DE_v decreases when the anion atomic number increases. We find that coupling between anion *p* and cation *d* states plays a decisive role in determining the absolute position of the valence band maximum and thus the observed chemical trends. © *1998 American Institute of Physics.* @S0003-6951~98!03316-6#

The offset D$E_v(AX/BY)$ between the valence ~v! band maxima of two semiconductor compounds AX and BY forming a heterostructure is one of the most important parameters in interfacial structures deciding both transport and quantum confinement. Extensive studies ~see review in Ref. 1! have been carried out in the past to both measure and calculate DE_v of II–VI and III–V semiconductor compounds. However, most of the experimental studies concerned only a particular pair and their results are somewhat scattered. Furthermore, many of the previous theoretical calculations involved approximations ~e.g., model solid,[2] no $p-d$ coupling,[3] etc.! whose validity has not been verified. Thus, overall regularities and trends were not apparent. In this letter we have systematically calculated the natural band offsets DE_v via *ab initio*, all-electron band structure method[4] between all II–VI

~i! Most valence band offsets are nonzero. This is in contrast with the ‘‘common-anion rule’’ [12,13,3] that suggested that the offset between two semiconductors having the same anion will be small. The smallest DE_v occur between Zn/Cd and Ga/In common-anion systems ~Table I!.

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ergy and higher cation *d* orbital energy!. Figure 2 shows schematically how the $p-d$ coupling affects the band offset:

~a! Trend ~