

Chapter 4

BAND ALIGNMENT FUNDAMENTALS: CHARGE DISTRIBUTION AND MODELING

4.1 Foundation of SBH and BO: Interface Charge Distribution

The difference in the CBMs of two semiconductors is known as the conduction band offset (CBO) at a heterojunction interface, while the valence band offset (VBO) is the offset in the VBM. Based on the signs of both band offsets for the same interface, the band alignment at a heterointerface can be distinguished into several types, as illustrated in Fig. 4.1.¹ The kind most commonly found experimentally is the type-I band alignment condition, where the smaller band gap lies entirely inside the band gap of the other semiconductor. When the two band gaps only partially overlap, the interface is said to display the type-II alignment condition. On occasions, one may even find no overlaps between the two band gaps and they lie completely outside of each other, shown as type III in Fig. 4.1. Type-III alignment is only seen at interfaces without intimate chemical bonds, such as those held together by van der Waals forces. At any interface between two insulators, the sum of the VBO and the CBO is a fixed quantity and equals the difference in the band gaps of the two materials. An increase in the VBO is accompanied by a decrease in the CBO, and vice versa. The offset in the energy band across a semiconductor interface plays a critical role in the operations of many advanced devices in microelectronics, photonics, energy harvesting, multiferroics, etc. Therefore, the factors that influence the magnitude of the BO need to be thoroughly understood in order to improve the performance of existing devices or to develop more advanced novel devices. However, investigations of BO formation at semiconductor heterojunctions should not be conducted in isolation because factors controlling BO formation are not fundamentally different from those for band alignment at other types of solid interfaces,