describe $CuInSe_2$ formation as a sequence of reactions starting with the formation of $Cu_{11}In_9$ and In liquid, which will contain a small concentration of dissolved Cu. These react with Se to form a series of binary compounds. The formation of $CuInSe_2$ then follows from

$$2\ InSe + Cu_2Se + Se \rightarrow 2\ CuInSe_2$$

with complete reaction in ~15 min at 400°C. The reaction path was shown to be the same for the reaction of Cu/In layers in either H_2Se or elemental Se [104].

The addition of Ga, regardless of the precursor deposition sequence, does not readily give a film with uniformly increased band gap. Instead, all Ga in the reacted film accumulates near the Mo forming a $CuInSe_2/CuGaSe_2$ structure, so the resulting device behaves like $CuInSe_2$ [105] and lacks the increased operating voltage and other benefits of a wider band gap discussed in Section 13.5.4. Nevertheless, Ga inclusion provides improved adhesion of the $CuInSe_2$ film to the Mo back contact and greater device performance, possibly owing to an improved structure with fewer defects [105]. The Ga and In can be effectively interdiffused, converting the films to uniform band gap, by annealing in an inert atmosphere for 1 h at 600°C [106]. This anneal, however, may be impractical for commercial processing, so films in the best devices have the band gap increased by the incorporation of S near the front surface, forming a graded $Cu(InGa)(SeS)_2$ layer [20, 107] that can give enhanced operating voltage in devices.

The primary advantages of two-step processes for Cu(InGa)Se_2 deposition are the ability to utilize more standard and well-established techniques for the metal deposition and reaction and anneal steps and to compensate for long reaction times with a batch processing mode or RTP of Se-containing precursors. Composition and uniformity are controlled by the precursor deposition and can be measured between the two steps. The biggest drawback to these processes is the limited ability to control composition and increase band gap, which may limit device and module performance. Other difficulties that must be overcome include poor adhesion and the use of hydrogen selenide, which is hazardous and costly to handle.

13.3.5 Other Deposition Approaches

$CuInSe_2$-based films have been deposited using a wide range of thin-film deposition methods, in addition to those discussed above, which have been proposed as potential low-cost alternatives for manufacturing. These include reactive sputtering [108], hybrid sputtering in which Cu, In, and Ga are sputtered while Se is evaporated [109], closed-space sublimation [110], chemical bath deposition (CBD) [111], laser evaporation [112], and spray pyrolosis [113]. Great effort was made to explore different thin-film deposition techniques before coevaporation and the two-step processes above became dominant. These methods are reviewed in Reference [25].

13.4 JUNCTION AND DEVICE FORMATION

The first experimental device that indicated the potential for $CuInSe_2$ in high-performance solar cells was a heterojunction between a *p*-type single crystal of $CuInSe_2$ and a thin film of *n*-type CdS [10, 11]. Consequently, in the early thin-film work the junction was