

in the temperature resulting from a change in the emissivity of the film [84] or by the infrared transmission [85].

The primary advantage of elemental coevaporation for depositing Cu(InGa)Se_2 films is its considerable flexibility to choose the process specifics and to control film composition and band gap. As proof of this flexibility, high-efficiency devices have been demonstrated using many process variations. The primary disadvantage results from the difficulty in control, particularly of the Cu-evaporation source, and the resulting need for improved deposition, diagnostic, and control technology. A second disadvantage is the lack of commercially available equipment for large-area thermal evaporation.

13.3.4 Two-step Processes

The second common approach to Cu(InGa)Se_2 film formation, usually referred to as two-step processing or selenization, has many variations in both the precursor deposition and the Se reaction steps. This general approach was first demonstrated by Grindle *et al.* [86] who sputtered Cu/In layers and reacted them in hydrogen sulfide to form CuInS_2 . This was first adapted to CuInSe_2 by Chu *et al.* [87]. The highest-efficiency Cu(InGa)Se_2 cell reported using the reaction in H_2Se is 16.2%, on the basis of the active area [88], but there has been less effort at optimizing laboratory-scale cell efficiencies than with coevaporated Cu(InGa)Se_2 . Showa Shell and Shell Solar have successfully scaled up this process to pilot commercial production and have demonstrated large-area module efficiencies as high as 13.4% [2].

The metal precursor is used to determine the final composition of the film and to ensure spatial uniformity. Sputtering is an attractive process because it is easily scalable using commercially available deposition equipment and can provide good uniformity over large areas with high deposition rates. However, other processes may have lower cost. CuInSe_2 has been formed using metal precursor layers deposited by electrodeposition [89], thermal or electron beam evaporation [90], screen printing [91], and application of nanoparticles [92]. Precursors that include Se, such as stacked layers of Cu/In/Se [93] or binary selenides, have also been used as precursor materials in various sequences and combinations [94]. Electrodeposition [95, 96] of Cu, In, Ga, and Se is effectively just another option for precursor deposition since the films similarly require a selenium reaction step.

The precursor films are typically reacted in either H_2Se or Se vapor at 400 to 500°C for 30 to 60 min to form the best device quality material. Poor adhesion [89] and formation of a MoSe_2 layer [97] at the Mo/ CuInSe_2 interface may limit the reaction time and temperature. Reaction in H_2Se has the advantage that it can be done at atmospheric pressure and can be precisely controlled, but the gas is highly toxic and requires special precautions for its use. The precursor films can also be reacted in a Se vapor, which might be obtained by thermal evaporation, to form the CuInSe_2 film [98]. A third reaction approach is rapid thermal processing (RTP) of either elemental layers, including Se, [99, 100] or amorphous evaporated Cu–In–Se layers [101].

The reaction chemistry and kinetics for the conversion of Cu–In precursors to CuInSe_2 has been characterized by X-ray diffraction of time-progressive reactions [102] and by *in situ* differential scanning calorimetry [103]. The results of these experiments