

much higher vapor pressure and lower sticking coefficient, so it is always evaporated in excess of that needed in the final film. Insufficient Se can result in a loss of In and Ga in the form of In_2Se or Ga_2Se [74].

Different deposition variations, using elemental fluxes deliberately varied over time, have been explored using coevaporation. Four different sequences that have been used to fabricate devices with efficiencies greater than 16% are shown in Figure 13.10. In each case, the targeted final composition is Cu-deficient with $\text{Cu}/(\text{In} + \text{Ga}) = 0.8 - 0.9$. The total deposition time may vary from 10 to 90 min, depending on the effusion rates from the sources. So, for a film thickness of 2 μm , typical deposition rates vary from 20 to 200 nm/min.

The first process is the simplest stationary process in which all fluxes are constant throughout the deposition process [75]. In most cases, however, the fluxes are varied using what is referred to as the Boeing process in which the bulk of the film is grown with Cu-rich overall composition so that it contains a Cu_xSe phase in addition to $\text{Cu}(\text{InGa})\text{Se}_2$ [15]. The fluxes are then adjusted to finish the deposition with In- and Ga-rich flux so that the final film composition has the desired Cu-deficient composition. One modification of this is the second process shown in Figure 13.10. This process was first implemented with CuInSe_2 films deposited on non-Na containing substrates at $T_{\text{SS}} = 450^\circ\text{C}$, producing films with increased grain size and improved device performance. The effect of Cu_xSe as a flux for enhanced grain growth at higher T_{SS} was proposed by Klenk *et al.* [76]. However, in devices containing Na and Ga and with $T_{\text{SS}} > 500^\circ\text{C}$, no difference was found in the device performance using films with Cu-rich or uniform growth processes [75].

The third process shown in Figure 13.10 is a sequential process in which the In and Ga are deposited separately from the Cu. This was first proposed by Kessler *et al.* [77] with the deposition of an $(\text{InGa})_x\text{Se}_y$ compound, followed by the deposition of Cu and Se until the growing film reaches the desired composition. The layers interdiffuse to form the $\text{Cu}(\text{InGa})\text{Se}_2$ film. A modification by Gabor *et al.* [78] allows the Cu delivery to continue until the film has an overall Cu-rich composition. Then a third step is added to the process in which In and Ga, again in the presence of excess Se, are evaporated to bring the composition back to Cu-deficient. The metals interdiffuse, forming the ternary chalcopyrite film. This process has been used to produce the highest efficiency devices [1]. The improved device performance has been attributed to a band gap gradient, which results from the Ga concentration decreasing from the Mo back contact to the film's free surface [19], and to improved crystallinity of the films [79].

The last process shown in Figure 13.10 is an in-line process in which the flux distribution results from the substrate moving sequentially over the Cu, Ga, and In sources. This was first simulated in a stationary evaporation system [80] and has subsequently been implemented by several groups in pilot manufacturing systems (see Section 13.6).

A reproducible coevaporation process requires good control of the elemental fluxes from each evaporation source. While the evaporation rates from each source can be controlled simply by the source temperature, this may not give good reproducibility, especially for the Cu source that is at the highest temperature. Open-boat sources in particular will not give reproducible evaporation rates. Consequently, direct *in situ* measurement of the fluxes is often used to control the evaporation sources. Electron impact spectroscopy [15], quadrupole mass spectroscopy [81], and atomic absorption spectroscopy [82] have all