

There has been relatively little effort devoted to devices on single-crystal CuInSe₂ since this early work, in part because of the difficulty in growing high-quality crystals [12]. Instead, nearly all the focus has gone to thin-film solar cells because of their inherent advantages. The first thin-film CuInSe₂/CdS devices were fabricated by Kazmerski *et al.* using films deposited by evaporation of CuInSe₂ powder along with excess Se [13]. However, thin-film CuInSe₂ solar cells began to receive a lot of attention when the first high-efficiency, 9.4%, cells were demonstrated by Boeing [14]. At the same time, interest in Cu₂S/CdS thin-film solar cells waned owing to problems related to electrochemical instabilities and many of these researchers turned their focus to CuInSe₂.

The Boeing devices were fabricated using CuInSe₂ deposited by coevaporation, that is, evaporation from separate elemental sources [15], onto ceramic substrates coated with a Mo back electrode. Devices were completed with evaporated CdS or (CdZn)S deposited in two layers with undoped CdS followed by an In-doped CdS layer that served as the main current-carrying material [15]. Throughout the 1980s, Boeing and ARCO Solar began to address the difficult manufacturing issues related to scale-up, yield, and throughput leading to many advancements in CuInSe₂ solar cell technology. The two groups pursued different approaches to CuInSe₂ deposition, which today remain the most common deposition methods and produce the highest device and module efficiencies. Boeing focused on depositing Cu(InGa)Se₂ by coevaporation, while ARCO Solar focused on a two-stage process of Cu and In deposition at a low temperature followed by a reactive anneal in H₂Se.

The basic solar cell configuration implemented by Boeing provided the basis for a series of improvements that have led to the high-efficiency device technology of today. The most important of these improvements to the technology include the following:

- The absorber-layer band gap was increased from 1.02 eV for CuInSe₂ to 1.1–1.2 eV by the partial substitution of In with Ga, leading to a substantial increase in efficiency [16].
- The 1- to 2- μm -thick doped (CdZn)S layer was replaced with a thin, ≤ 50 nm, undoped CdS and a conductive ZnO current-carrying layer [17]. This increased the cell current by increasing the short wavelength (blue) response.
- Soda lime glass replaced ceramic or borosilicate glass substrates. Initially, this change was made for the lower costs of the soda lime glass and its good thermal expansion match to CuInSe₂. However, it soon became clear that an increase in device performance and processing tolerance resulted primarily from the beneficial indiffusion of sodium from the glass [18].
- Advanced absorber fabrication processes were developed that incorporate band gap gradients that improve the operating voltage and current collection [19, 20].

From its earliest development, CuInSe₂ was considered promising for solar cells because of its favorable electronic and optical properties including its direct band gap with high absorption coefficient and inherent *p*-type conductivity. As science and technology developed, it also became apparent that it is a very forgiving material since (1) high-efficiency devices can be made with a wide tolerance to variations in Cu(InGa)Se₂ composition [21, 22], (2) grain boundaries are inherently passive so even films with grain sizes less than 1 μm can be used, and (3) device behavior is insensitive to defects at the junction caused by a lattice mismatch or impurities between the Cu(InGa)Se₂ and