formed by depositing CdS on the CuInSe₂ films [114]. The device was further developed to contain an undoped layer of CdS, followed by CdS doped with In, both deposited by vacuum evaporation [14]. This defined the device structure (see Figure 13.1), which is basically the same as is commonly used today since the doped CdS is functionally a transparent conductor. A performance gain was achieved by alloying the CdS with ZnS to widen the band gap [15]. Further improvement of the performance was achieved when the doped CdS layer was replaced with doped ZnO [115, 116]. The undoped CdS layer adjacent to the Cu(InGa)Se₂ film was reduced in thickness in order to maximize the optical transmission. Since ZnO has a wider band gap than CdS, more light is transmitted into the active part of the device, resulting in a current gain. A conformal and pinhole-free coating of this thin CdS layer is obtained by using chemical bath deposition to make the CdS buffer layer.

13.4.1 Chemical Bath Deposition

Chemical bath deposition (CBD) of thin-film materials can be viewed as a chemical vapor deposition (CVD) in the liquid phase instead of the gas phase. It is also referred to as solution growth. The method has been used in particular for chalcogenide materials such as PbS [117], CdS [118], and CdSe [119]. A variety of precursor compounds or ions can be used to deposit a specific compound.

Deposition of CdS buffer layers on $Cu(InGa)Se_2$ is generally made in an alkaline aqueous solution (pH > 9) of the following three constituents:

- 1. a cadmium salt; for example, CdSO₄, CdCl₂, CdI₂, Cd(CH₃COO)₂
- 2. a complexing agent; commonly NH₃ (ammonia)
- 3. a sulfur precursor; commonly $SC(NH_2)_2$ (thiourea).

The concentrations of the various components of the solution can be varied over a range and each laboratory tends to use its own specific recipe. One example of a recipe that is being used to fabricate state-of-the-art Cu(InGa)Se₂ solar cells is

- 1. $1.4\times1/10^3~M~CdI_2~or~CdSO_4$
- 2. 1 M NH₃
- 3. 0.14 M SC(NH₂)₂

The Cu(InGa)Se₂ film is immersed in a bath containing the solution and the deposition takes place in a few minutes at a temperature of 60 to 80°C. This can be done either by immersion in a room-temperature bath that subsequently is heated to the desired temperature or by preheating the solution. The reaction proceeds according to the formula

$$\text{Cd}(\text{NH}_3)_4{}^{2+} + \text{SC}(\text{NH}_2)_2 + 2 \text{ OH}^- \rightarrow \text{CdS} + \text{H}_2\text{NCN} + 4 \text{ NH}_3 + 2 \text{ H}_2\text{O}$$

In practice, the chemical bath deposition is typically done in the laboratory with a very simple apparatus consisting of a hot plate with magnetic stirring, a beaker holding the solutions into which the substrate is immersed, and a thermocouple to measure bath