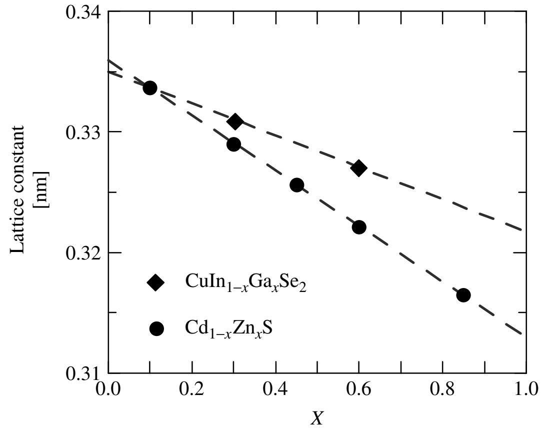

Figure 13.12 The lattice spacing of the (112) planes of $CuIn_{1-x}Ga_xSe_2$ and the (111) cubic or the (002) hexagonal planes of $Cd_{1-x}Zn_xS$. Empirical data from References [128] ((CdZn)S) and [129] ($CuInSe_2$, $CuGaSe_2$, and $(Cu(InGa)Se_2)$ are included

and 0.328 nm, respectively. Figure 13.12 displays the (112) spacing for $Cu(InGa)Se_2$ as a function of $Ga/(In + Ga)$ ratio together with the (111)/(002) spacing of CdS–ZnS alloys.

When $Cu(InGa)Se_2$ films are immersed in the chemical bath for deposition of CdS, they are also subjected to chemical etching of the surface. In particular, native oxides are removed by the ammonia [130]. Thus, the CBD process cleans the $Cu(InGa)Se_2$ surface and enables the epitaxial growth of the CdS buffer layer.

In early single-crystal work, *p–n* homojunction diodes were fabricated by indiffusion of Cd or Zn into *p*-type $CuInSe_2$ [131, 132] at 200 to 450°C. Investigations of $CuInSe_2$/CdS interfaces did show interdiffusion of S and Se above 150°C and rapid Cd diffusion into $CuInSe_2$ above 350°C [133]. More recently, intermixing of the constituents of the $Cu(InGa)Se_2$/CdS heterojunction has been observed even when the relatively low-temperature CBD process is used for growth of the CdS layer [134]. Investigations of the effect of a chemical bath without the thiourea showed an accumulation of Cd on the $Cu(InGa)Se_2$ surface, possibly as CdSe [130]. Accumulation of Cd on the $Cu(InGa)Se_2$ surface was also observed in the initial stage of CdS growth in the complete chemical bath [135]. The results were not conclusive on whether any interfacial compound is formed, but TEM investigations showed the presence of Cd up to 10 nm into the Cu-deficient surface region of the $Cu(InGa)Se_2$ layer [123]. At the same time, a reduction of the Cu concentration was noted. An interpretation in which Cu^+ is replaced with Cd^{2+} is proposed, on the basis of the very close ion radii of these ions, 0.96 and 0.97, respectively. XPS and secondary ion mass spectrometry (SIMS) profiles of $Cu(InGa)Se_2$ films and $CuInSe_2$ single crystals exposed to chemical baths without thiourea also show evidence of indiffusion or electromigration of Cd [136].

13.4.3 Other Deposition Methods

In the early days of $Cu(InGa)Se_2$ research, vacuum evaporation of 2 to 3-µm-thick CdS was the standard method to fabricate the junction and 9.4% efficiency was obtained with