

14.3.2 CdTe Absorber Layer and CdCl₂ Treatment

The large number of successful techniques for deposition of device-quality CdTe films was shown schematically in Figure 14.6. However, in cases of chloride-free deposition techniques such as physical vapor deposition (PVD), the actual deposition of the CdTe film has been found to be less critical than the postdeposition processing, which generally involves exposure to a high-temperature processing step followed by exposure to a chlorine-containing species and oxygen at $\sim 400^\circ\text{C}$, referred to as the “CdCl₂ treatment.” The treatment step has been performed in a variety of ways, such as dipping the CdTe layer in a CdCl₂:CH₃OH or CdCl₂:H₂O solution followed by drying to precipitate a CdCl₂ film [128, 129] by treatment in CdCl₂ vapor [130, 131] or by exposure to HCl [132] or Cl₂ gas [133]. Chlorine species may also be incorporated during CdTe film formation, in the form of Cl⁻ ions in an electrodeposition bath [134] or as a component of a screen-printing slurry [68]. The typical temperature–time range for the thermal cycle following chlorine incorporation is from 380 to 450°C for 15 to 30 min, depending on CdTe film thickness, with thicker films requiring longer treatment time.

The changes induced by chlorine incorporation and subsequent heat treatment depend on the prior thermochemical history of the CdTe/CdS structure. For example, the treatment can promote recrystallization and grain growth in films having submicrometer initial CdTe crystallite size [135]. The change in morphology and structure is shown in Figures 14.8 and 14.9. Figure 14.8 shows atomic force micrographs of the surface morphology of PVD CdTe, deposited at 250°C, before and after treatment at 420°C in CdCl₂ and air vapor. Figure 14.9 shows cross-sectional TEM images of changes in grain size and crystallographic defects in the junction region of a CdTe/CdS/ITO structure deposited by PVD onto a smooth Si wafer. Depositing the structure on a Si wafer facilitated the mechanical preparation of the sample for cross-sectional thinning. Table 14.2 more generally compares the changes in grain size, aspect ratio, and crystallite orientation for CdTe deposited by several different methods. For CdTe films having submicrometer initial crystallite size, such as shown in Figure 14.8, significant recrystallization occurs during the CdCl₂ treatment. This takes two forms: (1) intragrain, or primary, recrystallization changes grain orientation from typically (111) to random (see Figure 14.10) and (2) intergrain, or secondary, recrystallization results in grain coalescence. The phrase “fluxing agent” has been coined in reference to the role of CdCl₂ in promoting grain growth, although the secondary recrystallization does not always occur, depending on the thermochemical history of the film and the initial grain size. For films deposited at high temperature, having large initial grain size, annealed prior to CdCl₂ exposure, or containing the native oxide, CdTeO₃, little measurable grain growth (secondary recrystallization) occurs during CdCl₂ treatment. This is because surface energy is already minimized or is pinned by the presence of the oxide. Under these processing conditions, film randomization is the predominant effect, showing that CdCl₂ still exerts an intragrain influence on lattice arrangement.

The postdeposition treatment also modifies the electronic properties. Air-heat treatment alone, at temperatures above $\sim 500^\circ\text{C}$, can reduce the CdTe sheet resistance up to three orders of magnitude [136]. Treatment with CdCl₂ in air likewise reduces resistivity, by the combination of recrystallization and creation of acceptor states. The primary electronic effect of Cl incorporation seems to be the formation of an acceptor complex with Cd vacancies (see Figure 14.5). Both the single-donor and the double-acceptor states are