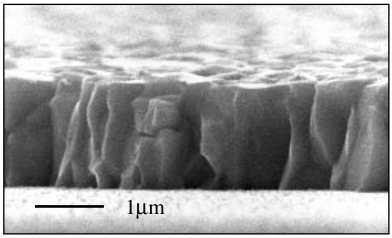

Figure 13.8 Scanning electron microscopy image of a typical Cu(InGa)Se_2 film deposited on a Mo-coated glass substrate by coevaporation

have grain diameters on the order of 1 μm but the grain size and morphology can vary greatly depending on fabrication method and conditions. A variety of defects including twins, dislocations, and stacking faults have been observed [49–51].

It has been shown by X-ray photoelectron spectroscopy (XPS) that the free surfaces of $CuInSe_2$ films with slightly Cu-poor composition have a composition close to $CuIn_3Se_5$ [52], corresponding to one of the ordered defect phases. Many attempts have been made to identify such a layer on top of the films without success. It merely seems as if the composition gradually changes from the bulk to the surface of the films. It was proposed by Herberholz *et al.* [35] that band bending induced by surface charges drives electromigrating Cu into the bulk leaving the surface depleted of Cu. This depletion is stopped when the composition is that of $CuIn_3Se_5$, since further depletion requires a structural change of the material. Electromigration of Cu in $CuInSe_2$ has been demonstrated and also correlated with type conversion of the chalcopyrite material [53].

The band bending as well as the $CuIn_3Se_5$ composition of $CuInSe_2$ surfaces disappears when the material is exposed to atmosphere for some time as oxides form on the surface. The surface oxidation is enhanced by the presence of Na [39]. The surface compounds after oxidation have been identified as In_2O_3, Ga_2O_3, SeO_x, and Na_2CO_3 [54]. A review of the surface and the interface properties can be found in Reference [55].

It has been common practice to posttreat Cu(InGa)Se_2 devices in air at typically 200°C. When devices were fabricated using vacuum-evaporated CdS or (CdZn)S to form the junction, these anneals were often done for several hours to optimize the device performance [14, 56]. The main effect associated with oxygen is explained as passivation of selenium "surface" vacancies on the grains [57]. The V_{Se} at the grain boundaries can act as a recombination center. The positive charge associated with these donor-type defects reduces the effective hole concentration at the same time that the intergrain carrier transport is impeded. When oxygen substitutes for the missing selenium, these negative effects are canceled.

The overall noted beneficial effect of the presence of Na on the PV performance of Cu(InGa)Se_2 thin films lacks a complete explanation. In Reference [58] it is proposed that the catalytic effect of Na on oxidation, by enhanced dissociation of molecular oxygen into atomic oxygen, makes the passivation of V_{Se} on grain surfaces more effective. This model is consistent with the observation that Na and O are predominantly found at the grain boundaries rather than in the bulk of the grains in $CuInSe_2$ thin films [59].