Table 13.3 Performance of $Cu(InGa)Se_2$ thin-film solar cells with various buffer layers and junction-formation methods alternative to chemical bath deposition of CdS

Buffer material	Deposition method	Efficiency [%]	V_{OC} [mV]	J_{SC} [mA/cm^2]	FF [%]	Reference
None		10.5[a]	398	39.0	68	[139]
None		15.0[b]	604	36.2	69	[1]
ZnO	MOCVD	13.9[a]	581	34.5	69	[140]
ZnO	ALCVD	11.7	512	32.6	70	[141]
Zn treatment	$ZnCl_2$ solution	14.2[b]	558	36.3	70	[142]
$Zn(O,S,OH)_x$	Chemical bath	14.2[c,d]	567[e]	36.6[e]	68	[143]
ZnS	Chemical bath	16.9[a,b]	647	35.2	74	[144]
Zn treatment + ZnS	Chemical bath + ILGAR[f]	14.2	559	35.9	71	[145]
Zn(Se,OH)	Chemical bath	13.7[b,d]	535	36.1	71	[146]
ZnSe	ALCVD	11.6[a]	502	35.2	65	[147]
ZnSe	MOCVD	11.6	469	35.8	69	[148]
In_xSe_y	Coevaporation	13.0[a]	595	30.4	72	[149]
$ZnIn_xSe_y$	Coevaporation	15.1	652	30.4	76	[150]
$In_x(OH,S)_y$	Chemical bath	15.7[a,b]	594	35.5	75	[151]
In_2S_3	ALCVD	13.5	604	30.6	73	[152]

[a] Active area
[b] With antireflection layer
[c] Minimodule
[d] Confirmed
[e] Recalculated to single-cell values
[f] Ion Layer Gas Reaction

When the numbers in Table 13.3 are analyzed, one must keep in mind that the quality of the $Cu(InGa)Se_2$ layer varies significantly between the experiments. For example, in the early results with direct ZnO [139], the reference cells with chemical bath–deposited CdS showed 12.4% efficiency, whereas the 15% efficiency results [1] are obtained from $Cu(InGa)Se_2$, which at best yielded an efficiency of 18.8%. On the other hand, an inferior junction-formation method may cause a larger degradation of cell efficiency at higher efficiency levels, since its defects may be relatively more important to the cell performance. In order to evaluate the various Cd-free junction-formation methods from that respect, the efficiency from each experiment is displayed in Figure 13.13 together with its reference, or estimation thereof. In most cases, the Cd-free device is comparable to the CBD–CdS device within typical variations.

Altogether, it appears as if there are several possibilities for obtaining high efficiency without Cd. All the listed methods include one or more of the elements Zn, In, and S. Zn is directly included in most of the buffer materials or indirectly as ZnO transparent contact with In_xSe_y, $In(OH,S)_x$, and In_2Se_3. Indications that n-type doping with Zn occurs similarly to that with Cd have been found by the treatment of $Cu(InGa)Se_2$ in Cd and Zn solutions [136], and are consistent with junction formation by solid-state diffusion into single crystals [132].

In Figure 13.13 a slight tendency can be noted toward larger difference between Cd-free and CdS reference cells for the direct ZnO approaches. It appears as if a buffer layer between the $Cu(InGa)Se_2$ and the ZnO is beneficial. Such a layer could passivate the