INTRODUCTION

Photovoltaics (PV) using thin film CdTe as a photon absorber have been studied for several decades. CdTe was long recognized for its potential to surpass the conversion efficiencies of conventional silicon solar cells based on bandgap matching to the Shockley Queisser limit. \(^1\) However, progress was slow in reaching this protentional with best laboratory cell efficiencies climbing from ~9% in 1976 to 16% in 1993. \(^2,3\) A virtual plateau in efficiency followed for the next 20 years before the efforts of First Solar and GE Global Research (now one entity) helped push the efficiency to 22.1% at the time of this review by the First Solar company. \(^2,4,5\) First Solar are the leading commercial manufacturers of thin film photovoltaics having recently introduced their Series 6 offering in excess of 17% efficiency at the module level. \(^5,6\)

CdTe PV can be constructed under two device architectures (Figure 1); the PV thin films can be deposited onto a substrate material in the general order electrode, p-type CdTe absorber, n-type buffer layer, electrode or the reverse order.
transparent substrate material, transparent electrode, n-type buffer, p-type CdTe absorber, and electrode. The latter is the preferred route for several optimal device performance reasons and necessitates the use of an optically transparent superstrate material and initial electrode layer. The CdTe in superstrate configuration relies on the following factors, among others, to achieve high conversion efficiency. Firstly, a substrate, electrode (front contact), and n-type buffer which are optimized to transmit photons with an energy above the absorber bandgap. Secondly, a chlorine heat treatment of the CdTe and thirdly, an Ohmic (back) contact to the CdTe. The majority of CdTe PV research and all module manufacturing to date has exploited the superstrate configuration.

CdTe has a high electron affinity of around 4.4 eV, which together with its energy gap of around 1.45 eV, means that many materials that might be considered good conductors and thus good back contacts, tend to form Schottky barriers (see Figure 2A) which oppose the flow of current into the solar cell.

The exceptions to this are metals with very high work functions which form Schottky contacts with small barriers and can thus act effectively as Ohmic-like contacts at normal working temperatures (eg, gold and palladium). This difficulty has been noted many times (eg, Wald (1977), Fahrenbuch (1987)). Demtsu and Sites (2006) gave a good description of how forward-bias rollover can occur due to a rear contact barrier.

Before we consider the multitude of possible back contacts, it is important to note that the chemistry of the materials at and near the back contact needs to be considered as much as the fundamental physical properties of CdTe and its back-interface material. The interface must minimize photogenerated carrier recombination. The simplistic approach of matching the valence band positions through knowledge of a value of the electron affinity and the bandgap, although useful, can also be misleading if the chemistry leads to interlayer compound formation, or interfacial states lead to Fermi level pinning.

The back contact issue is not unique to CdTe—it is also believed to be a limiting factor in some other thin film solar cell technologies; such as the perovskite structure materials (“ABX₃” which achieve high efficiency but are not yet a well-established commercial technology), and other thin film solar cell technologies using chalcogenides (mainly CIGS and kesterites). The back contact is also commonly referred to as the hole transport material (HTM) in perovskites.
and is one factor limiting both efficiency and long-term stability\textsuperscript{15} of perovskite devices.

Many CdTe back contact technologies utilize small amounts of copper to increase the p-type doping level. This element can be delivered as a metal layer with a thickness of a few nanometers, or as a copper compound, such as Cu$_2$Te. Thicknesses of copper-containing layers is often well below 10 nm. However, it is known that as well as providing p-type doping copper introduces deep levels\textsuperscript{16} into the CdTe, and that copper is highly soluble in CdTe.\textsuperscript{17} Copper re-distribution within a polycrystalline solar cell is a complex process. However, the record efficiency cells have almost unanimously utilized copper as part of their back contact technology.

The challenge of creating an optimum back-surface contact for CdTe has been a goal of many research teams for decades and has been reviewed before, for example by McCandless and Sites (2011)\textsuperscript{18} and Kumar and Rao (2014).\textsuperscript{19} This review seeks to integrate post-2014 literature into a comprehensive view of the subject.

Back contact technologies for polycrystalline CdTe on flexible substrates have recently been reviewed by Znajdek et al (2019).\textsuperscript{20} A small number of back contact technologies were reviewed in this paper, before copper, molybdenum, and silver (full coverage of silver and a mesh) were used in bending test experiments. In the case of flexible cells, adhesion and matching of thermal expansion coefficients are even more crucial than when CdTe is deposited on rigid substrates.

In reviewing the literature for back contacts to CdTe, it seemed prudent to the authors to group the many materials that have been used into categories. However, it is acknowledged that the categorization used here is not unique. Neither does it adequately describe the multiple materials and processes used in many cases. Nevertheless, it can be a useful approach. The list of categories used is given in Table 1.

In this analysis, it is often difficult to do like-for-like comparisons. Devices with deliberately grown Cd(Se,Te) absorbers will have a different point at which solar cell performance is strongly limited by the back contact, due to effects such as different front contact, carrier lifetimes, and grain boundary passivation. Consequently, such devices are largely excluded from the analysis, except when little or no information is available for a back contact material with a CdTe absorber. CdTe n-type absorber solar cells are not included in this review due to the comparatively little literature available. Differences in the front contact are also present. Often the difference in the front contact will largely affect the short-circuit current. Therefore, power conversion efficiency (PCE), open-circuit voltage ($V_{oc}$), and fill factor (FF) will be given more consideration.

In some cases, it is arguable as to whether a process treatment also can be classified as a back contact material. One important example is the ubiquitous chlorine heat treatment (CHT) (most commonly using CdCl$_2$ or chlorine diffusion). If this treatment leaves the back-surface rich in chlorine, then chlorine can be said to be a constituent of the back contact material, even though a further material will be required for electrical contact.

A second classification of back contact materials is whether the process is free of copper (or other potentially mobile dopants) or not. As mentioned, a small amount of copper has been an integral part of many of the back contact technologies developed for CdTe solar cells. Copper is commonly used to dope CdTe p-type to a suboptimal doping level in the range $10^{14}$ to $10^{15}$ cm$^{-3}$. However, the presence of “excess” copper is also associated with long-term cell degradation.\textsuperscript{21} Therefore, many of the copper-containing processes have undergone trials with very restricted amounts of copper to optimize performance, but also to minimize long-term performance drops. Other approaches have sought a copper-free contacting technology.\textsuperscript{22} It is not within the scope of this paper to review all the literature on copper usage in back contact technologies, itself the subject of many articles.\textsuperscript{23}

A third possible classification is whether the contact material(s) are transparent. (It is noted that CdTe is not transparent in the visible spectrum for absorber layers thick enough to produce high PCE). As shown in Figure 1 the superstrate

### Table 1: Categories of materials used in back contacts to CdTe solar cells and shorthand notations for the principal components considered within that category

<table>
<thead>
<tr>
<th>Category</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group IV</td>
<td>a-Si:H, a-Si$_{1-x}$C$_x$:H, Bi-RGO</td>
</tr>
<tr>
<td></td>
<td>CuCNI, Cu$_2$Te/SWCNT, graphene:B, SWCNT, graphite</td>
</tr>
<tr>
<td>Metal</td>
<td>AgNW/ITO, Cu, Cu NW, Mo</td>
</tr>
<tr>
<td>Metal pnictide</td>
<td>Mo$_x$N$_y$, Zn$_x$N$_y$P</td>
</tr>
<tr>
<td>Metal oxide</td>
<td>Cu$_x$O/Au, CuO$_x$ ITO, Cu/Au/ZnO:Al</td>
</tr>
<tr>
<td></td>
<td>MoO$_x$, MoO$_2$, MoO$_3$:Cu NiO (p-type), $V_x$O$_y$, WO$_3$, ZnO:Al</td>
</tr>
<tr>
<td>Metal selenide</td>
<td>VSe$_2$, TiSe$_2$, (BaCuSeF, SrCuSeF)</td>
</tr>
<tr>
<td>Metal sulfide</td>
<td>CIS, CIS:N, CuS, CuS/ZnS, FeS$_2$, (Fe,Ni)$_2$S$_2$</td>
</tr>
<tr>
<td>Metal telluride</td>
<td>Cu$_x$Te, Cu$_x$Ni, HgTe:Cu, NiTe$_2$, SnTe:Ni ZnTe:Cu, ZnTe:Cu/ITO, ZnTe:N-ITO, ZnTe:Se</td>
</tr>
<tr>
<td>Telluride, other</td>
<td>(N$_2$H$_4$)$_2$CdTe$_2$, Cs$_2$CdTe$_2$, K$_2$CdTe$_2$, Na$_2$CdTe$_2$, As$_2$Te$_3$, Sb$_2$Te$_3$, Bi$_2$Te$_3$</td>
</tr>
<tr>
<td>Metal halides and perovskites</td>
<td>CuI, BaCuSeF, SrCuSeF, BaCuSF, BaCuSF/ITO, MAPb$_{1-x}$Pb$_x$Br$_y$</td>
</tr>
<tr>
<td>Organic and carbon containing</td>
<td>CuPc/Au, CuSCN/Au P3HT, PCBM, PEDOT, Pentacene, PFO, Ppy, spiro-OMeTAD</td>
</tr>
</tbody>
</table>
configuration transmits photons to the absorber layer via the transparent substrate, front contact, and n-type buffer. However, for some applications such as tandem and bifacial solar cells, a contact with good visible and near-infrared transparency to at least 800 nm is also required. A third technology which requires NIR transparent back contacts is a nonconventional PV-thermal (PVT) solar cell in which the transmitted NIR radiation is used elsewhere, including by focusing NIR onto a heat collector such as an evacuated tube. For these architectures, any use of narrow bandgap materials, or metals thicker than 10 nm or so, at the back surface will reduce substantially transmission of subbandgap radiation through the CdTe. If back contact materials are extremely thin, or do not have close to 100% coverage of the back surface, then a binary transparent/opaque description could be misleading.

The maximum processing temperature during the deposition of back contacts needs to be considered. Although CdTe has a high melting point (1050°C), some elements can diffuse quickly through CdTe. In polycrystalline CdTe, diffusion along grain boundaries can be much faster than bulk diffusion (eg, copper and sulfur). Grain boundary passivation from the CHT process can also be affected by loss of Cl at very high subsequent processing temperatures.

The metal(s) used as the final contact also influence PCE in some cases, as well as sometimes making the devices more or less stable over time. This can be through the formation of Schottky barriers or by diffusion into or through the CdTe.

To maximize solar cell PCE, resistive heating losses need to be minimized. If a back contact material has a low lateral conductivity, then a more conductive layer is required on top to avoid excessive series resistance. Conductive materials dominated by hopping conductivity, such as many organic compounds, have very low mobility values compared to relatively large-grained inorganic conductors with delocalized conduction or valence bands. These low mobility materials will always require a more conductive layer on top, or a metal grid/mesh/network with low mean spacing, so lateral transport to a metal is only a short distance.

Although it has been stated that band offsets are of limited use, the concept is of some use in choosing materials to study. Directly measuring band offsets is difficult. XPS studies can give a picture of offsets relative to vacuum level, but less so when buried within a device structure. Analysis of temperature-dependent forward-bias rollover in J-V curves is one method of determining an effective back contact barrier in situ and inferring valence band offset (VBO).

Recently, the concept of initial Fermi level offset (IFLO) has been promoted (Liyanage et al (2019)) through extensive 1-D modeling (using SCAPS); this concept might allow doping levels in CdTe and the back contact material to be accounted in a better manner than just using the VBO.

### 2. Surface Processing Before Back Contacts

#### 2.1 Chemical treatments

Chemical treatments prior to back contact deposition have been reviewed by Kumar and Rao (2014). The as-grown CdTe can be subject to chemical modification by etching prior to back contact deposition. It is noted that the presence of many grain boundaries in polycrystalline CdTe means that some etches which might provide a beneficial surface condition on single-crystal CdTe might increase recombination at grain boundaries on polycrystalline CdTe.

The first etch we mention is an etch using potassium chromate and sulfuric acid (chromate etch) used on p-type bulk-grown CdTe. Anthony et al (1982) measured contact resistances of 0.1-0.5 Ω cm² using Cu-Au or Au on a K₂Cr₂O₇·H₂SO₄ etched surface—significantly lower than when a bromine-methanol (Br-Me) etch was used. This etch leaves the surface Te-rich with the presence of some TeO₂. Rimmaudo et al (2017) attempted to form a layer of Cu₂Te through a process including Br-Me etching before Cu/Au deposition. The Br-Me etch allowed less Cu to be used, giving a “more optimal” doping and improving device stability. Improved performance was also attributed to the reduction in grain roughness observed in AFM studies. Awni et al (2018) and (2019) also showed grain roughness reduction when using a hydrogen iodide in methanol etch. Additionally, a reduction in back contact barrier height was observed after etching.

Another common etch is a nitric-phosphoric (NP) etch. Both Br-Me and NP etches leave the surface Te-rich; the NP etch leaves a thicker Te-rich layer. A Te-rich surface is believed to be beneficial for back contact formation. The NP etch preferentially etches grain boundaries and can be overdone, leading to pinholes. Proskuryakov et al (2007) studied various NP etch conditions using both solar cell J-V characteristics and variable temperature admittance spectroscopy. Short etch times mostly affected the back surface, but longer etch times also caused changes at grain boundaries. Major et al (2014) (Liverpool University) used N-P etches before and after chloride treatments in a study of chloride treatments other than CdCl₂ (MgCl₂, NaCl, KCl, and MnCl₂).

#### 2.2 Electron reflectors

Hole transport is required at the back contact of a superstrate CdTe solar cell. Electrons which reach the back contact interface are likely to recombine. Hsiao and Sites at Colorado State University studied strategies for providing interfaces with an electron reflecting character, reducing interface...
recombination. The introduction of a material with a small valence band offset and a larger conduction band (likely higher energy gap) could provide a means for hole transport, while band bending at the interface could lead to an electric field tending to repel electrons from the interface (“reflection”). A generic alignment of conduction and valence bands for an electron reflector back contact is shown in Figure 2C. Hsiao and Sites work suggested that PCE 19%-20% was possible with a 1 µm thick absorber if an electron reflector was used in a structure which also had good optical reflection. ZnTe is an early example of a material with the expected band alignment expected to produce electron reflection when deposited on CdTe. More recently other materials including CdMgTe have been studied as potential electron reflectors.

3 | METAL BACK CONTACTS

Metals tend to form Schottky contacts to p-type CdTe, as indicated by Ponpon (1985) (see Figure 2A). The lowest barriers are formed with high work function metals, nickel (see nickel telluride contacts), and gold, which are a closer match to the electron affinity plus bandgap of CdTe. Gold and platinum are too expensive for use in modules but can be very useful in laboratory studies. Of the economically viable metals, only nickel (and carbon) has work functions sufficiently high to avoid very large Schottky barriers. Nickel in CdTe forms a deep acceptor level.\(^4\) One example paper (Wei Xia et al (2014)\(^4\)) shows the effect of using Ni on as-grown CdTe surfaces: PCE is improved by NP etching before Ni deposition, or by using Te or Te/Cu interlayers before Ni deposition. For long-term stability, the diffusion of metals into CdTe must be considered.

In many cases, tellurides can form at the interface when metals are deposited. The effect of the tellurides on the interface needs to be considered (see also the section on telluride contacts). Even less reactive metals such as gold can form a telluride at the interface. Odkhuu et al (2016)\(^4\) performed electronic structure calculations on the Schottky barriers formed between CdTe and Cu, Pt, and Al when the CdTe surface was Cd-terminated and Te-terminated. Different barrier heights were obtained for the different surface terminations, and barrier heights were found to be heavily influenced by metal-induced gap states. Li et al (2017)\(^4\) also studied Schottky barrier heights for Al, Ag, Au, Cu, and Ni. The lowest Schottky barriers determined were Ni (0.66 eV) and Au (0.44 eV).

4 | TELLURIUM AND TELLURIDE BASED CONTACTS

In this category the following materials that have been used for back contacts will be discussed: tellurium, undoped and doped copper tellurides, mercury telluride, nickel telluride, tin telluride, with a more extensive discussion on zinc telluride and its doping.

4.1 | Tellurium as a back contact

Tellurium is one natural choice of back contact, as the element is already present in the CdTe absorber. The melting point is much lower than CdTe at around 450°C. Tellurium is a (bulk) p-type degenerate semiconductor with reasonably high conductivity that can be increased by doping (copper) and has a low VBO to CdTe.\(^5\)

Niles et al (1996)\(^4\) showed a PCE value of 12.1% with an evaporated Te back contact (\(V_{oc} 740 \text{ mV}, J_{sc} 22.4 \text{ mA cm}^{-2} \text{ FF} 65.4\%\)), slightly outperforming their control process which involved etching to obtain a Te-rich surface. A near contemporaneous XPS study by Niles et al (1995)\(^4\) had found a valence band offset of 0.26 ± 0.1 eV between the evaporated Te and CdTe. Kraft et al (JAP 2003)\(^9\) found a valence band offset of ~0.5 eV using XPS between CdTe and Te prepared by chemical etching of CdTe. Moffet and Sampath (2017)\(^5\) published XPS characterization work on Te thickness variations on CdTe. Temperature-dependent J-V curves showed the back-barrier height decreasing as Te thickness increased from 2 nm to 8 nm, reaching bulk values at 50 nm.

Tellurium back contacts were one component of the revised structure (Munshi et al (2018)\(^5\) (Colorado State University) used to achieve a cell with 18% PCE They also used a Mg\(_x\)Zn\(_{1-x}\)O buffer, thick CdTe, and front AR coating. The back contact barrier height was suggested by Alfadhili et al (2019)\(^5\) to be smaller for Te than for ZnTe.

Provision of a deposited Te layer has produced higher PCE than a Te-rich layer produced by etching as the Te layer thickness is more controllable in a deposition process, as well as avoiding the possible creation of etched pinholes and affecting passivated grain boundaries.

4.2 | Copper telluride

Copper telluride introduces copper which will dope CdTe\(^5\) and provide the back contact. Ferekiades et al (1997)\(^5\) showed PCE values approaching 15%. They found that a thin (50 nm) copper telluride layer produced maximum \(V_{oc}\) and FF (best Cu\(_x\)Te/Mo back contacted cell: PCE 14.9%, \(V_{oc} 838 \text{ mV}, J_{sc} 23.77 \text{ mA cm}^{-2}, \text{FF} 74.95\%—\text{NREL certified}.\) McCandless et al (2003)\(^5\) investigated the different phases of copper telluride formed on the back surface following the deposition of different thicknesses of copper. Yan et al (2005)\(^5\) at NREL published on the use of copper telluride. In this case, HgTe was used as well, forming HgCdTe at the back surface, so the role of copper telluride itself is more difficult
to extract. It was also investigated by Avachat (2005)\textsuperscript{56} of the University of Central Florida, Wu et al (2007),\textsuperscript{57} and Zhou et al (2007),\textsuperscript{58} who found that the dominant phase of copper telluride was thickness dependent, becoming more copper rich with increasing thickness. The maximum PCE (12.9%, $V_{oc}$ 797 mV, $J_{sc}$ 22.7 mA cm$^{-2}$, FF 71.3%, and $R_s$ 1.09 $\Omega$ cm$^{-2}$) was obtained at a copper telluride thickness of 10 nm (mixed CuTe and Cu$_{1.4}$Te phases), while at a thickness of 60 nm, the PCE dropped to 12.1% (single-phase Cu$_{1.4}$Te). At a thickness of 130 nm, the less thermodynamically stable Cu$_2$Te phase dominated but at a thickness of 10 nm, the PCE dropped to 12.1% (single-phase Cu$_{1.4}$Te). More recently, Moore (2017)\textsuperscript{59} studied CdTe interface,\textsuperscript{60} but the ZnTe is also expected to reduce or via grain boundaries to form copper tellurides at the ZnTe—CdTe interface,\textsuperscript{61} but the ZnTe is also expected to reduce or slow diffusion of copper into the CdTe.\textsuperscript{61}

Back surface processes that deposit thin layers of copper on Te-rich surfaces also form copper tellurides and, in some cases, the formation of copper tellurides can act as a means of consuming excess copper which could otherwise diffuse through the CdTe. It has also been suggested that copper deposited on top of other layers (specifically ZnTe) can diffuse via grain boundaries to form copper tellurides at the ZnTe-CdTe interface,\textsuperscript{60} but the ZnTe is also expected to reduce or slow diffusion of copper into the CdTe.\textsuperscript{61}

### 4.3 | Mercury telluride and Hg$_{1-x}$Cd$_x$Te

Mercury (II) telluride (HgTe) is a semi-metal rather than a semiconductor. It has a relatively high conductivity compared to CdTe. Hg$_{1-x}$Cd$_x$Te alloys are stable with a cubic crystal structure with a nearly constant lattice parameter for all compositions.\textsuperscript{62} The low energy gap means that the material is not transparent in the near infrared (NIR) until the CdTe composition exceeds around 70%. Hg$_2$Te bonds are relatively weak compared to Cd$_2$Te bonds leading to Hg diffusion at moderately high temperatures.

Janik and Triboulet (1987)\textsuperscript{62} showed that HgTe deposited by close space sublimation could provide a low resistance Ohmic contact to CdTe and Hg$_{1-x}$Cd$_x$Te, due to good work function matching, but did not fabricate solar cells. This work was extended by Zozime and Vermeulin (1988)\textsuperscript{63} to analyze specific contact resistance accounting for doping level. Specific contact resistance remained at 15-500 $\Omega$ cm$^2$ for material of resistivity 1.5-45 $\Omega$ cm but dropped to 7 $\Omega$ cm$^2$ for ~70 $\Omega$ cm resistivity material.

A paste made of graphite mixed with HgTe (often copper doped) has been used extensively\textsuperscript{64,65} and probably was the material used by Britt and Ferekides (1993)\textsuperscript{3} in their 15.8% PCE device ($V_{oc}$ 843 mV, $J_{sc}$ 25.1 mA cm$^{-2}$, FF 74.5%). A CuTe:HgTe doped graphite paste (then silver paste) was used by Wu et al (2001)\textsuperscript{66} in NREL’s then record 16.5% PCE device ($V_{oc}$ 845 mV, $J_{sc}$ 25.9 mA cm$^{-2}$, FF 75.5%), this device had cadmium stannate/zinc stannate front contacts.

Hanafusa et al (2001)\textsuperscript{67} used a wide range of materials to “dope” graphite pastes used as back contacts. The added materials that resulted in PCE over 12% included the silver halides (AgCl and AgF), silver telluride, silver phosphate and molybdate, as well as nickel phosphide and telluride, and zinc phosphide. Lead-containing additives reduced PCE, as did NiO. Compounds containing Bi and Sb were also tried.

#### 4.4 | Zinc telluride

Zinc telluride (ZnTe) is a semiconductor with an ambient temperature energy gap of around 2.2 eV,\textsuperscript{68} higher than the energy gap of CdTe. ZnTe has the same cubic crystal structure as CdTe. The high bandgap means that ZnTe is not suitable for use as a single absorber in a high PCE solar cell. ZnTe can be doped p-type by pnictides (N,\textsuperscript{69} P,\textsuperscript{70} As,\textsuperscript{71} Sb,\textsuperscript{72} and Bi) and by copper. The electron affinity of ZnTe is such that the valence band offset to CdTe is very low.\textsuperscript{73} This allows hole transport to a metal contact with smaller barriers than for those created by directly contacting CdTe with metals. There are also suggestions that ZnTe could act as an electron reflector if the recombination rate at the interface is sufficiently low (see also section on electron reflectors).

ZnTe was the contact material to CdTe for AMETEK’s late 1980s world record ITO/CdS/CdTe/ZnTe/Ni solar cell which achieved PCE 11%. Copper-doped ZnTe on CdTe has been studied since before 1992 (Mondal et al (1992)\textsuperscript{74} at the University of Delaware) and by many groups since. By 2015,

<table>
<thead>
<tr>
<th>Reference</th>
<th>Material</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>$R_s$ ((\Omega) scm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferekides et al (1997)\textsuperscript{54}</td>
<td>CdS/CdTe/Cu$_{1.4}$Te/Mo</td>
<td>838</td>
<td>23.8</td>
<td>74.9</td>
<td>14.9</td>
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<tr>
<td>Xia et al (2014)\textsuperscript{64}</td>
<td>CdS/CdTe/Cu</td>
<td>820</td>
<td>22.2</td>
<td>77.6</td>
<td>14.1</td>
<td>-</td>
</tr>
<tr>
<td>Zhou et al (2007)\textsuperscript{58}</td>
<td>CdS/CdTe/Te/NP etch/Cu/C-paste/Ag</td>
<td>797</td>
<td>22.7</td>
<td>71.3</td>
<td>12.9</td>
<td>1.09</td>
</tr>
<tr>
<td>Kim et al (2018)\textsuperscript{236}</td>
<td>ITO/Cds/CdTe/Cu$_2$Te</td>
<td>~800</td>
<td>25.5</td>
<td>59</td>
<td>~12</td>
<td>6.5</td>
</tr>
<tr>
<td>Moore (2017)\textsuperscript{59}</td>
<td>CdS/CdTe/Cu/Te/Ni</td>
<td>801</td>
<td>22.4</td>
<td>72.4</td>
<td>13.0</td>
<td>1.1</td>
</tr>
<tr>
<td>Moore (2017)\textsuperscript{59}</td>
<td>MgZnO/CdTe/Cu/Te/Ni</td>
<td>853</td>
<td>25.7</td>
<td>77.9</td>
<td>17.1</td>
<td>0.6</td>
</tr>
</tbody>
</table>
NREL reported a 16.4% PCE, although the focus of this paper was the fact that the CdTe solar cell was flexible.

Amin et al (2002) tried ZnTe and Cd$_{0.7}$Mg$_{0.3}$Te:N back contacts to thin (1 µm CdTe) solar cells obtaining 8.3% PCE (low FF of 49%) for ZnTe/Cu/Ag contacted devices. Chen et al (2019) studied ZnTe:Cu back contacts to CdTe using a CdSe buffer layer (ITO/ZnO/CdSe/CdTe/ZnTe/Cu/Au structure). Although an improvement over the Au only back contact was observed, the maximum PCE was 6.38%.

A ZnTe-based back contact layer still requires metallization. Gessert et al (2014) studied the contact properties of titanium on doped ZnTe. Metal-semiconductor contact resistance is a somewhat neglected area of study in the context of CdTe solar cells (and associated materials): a comprehensive review is overdue but is not within the scope of this article. Gessert et al concluded that the likely range of contact resistance of Ti to ZnTe was 0.1-0.5 Ω cm$^2$. This is orders of magnitude more than can be achieved with rare metal contacts such as between Au on Pd on >10$^{19}$ cm$^{-3}$ p-doped ZnTe (5 $\times$ 10$^{-6}$ Ω cm$^2$ - Ozawa et al (1994)).

Kurley et al (2017) used liquid chemistry to modify the rear surface of CdTe solar cells. This approach is categorized here with the ZnTe papers for convenience but is really a distinct approach. The best PCE (12.7%) resulted from forming an interfacial layer of (N$_2$H$_5$)$_2$CdTe$_2$ on top of CdTe. This was a marginal PCE gain over their control device with $V_{oc}$ improved from 684 mV (control) to 726 mV ((N$_2$H$_5$)$_2$CdTe$_2$ treated). Another contact used by Kurley was to spin-coat ZnTe:Sb onto CdTe (best cell PCE 6.4%).

It is clear from Table 3 that in order to obtain high PCE either the back contact process must contain Cu or the CdTe is already heavily p-type doped (Oklobia et al (2019) used arsenic doping).

Cd$_{0.7}$Mg$_{0.3}$Te was recently used by Feng et al (2020) to increase the conduction band offset at the back interface while not creating a large VBO. A Cd$_{0.7}$Mg$_{0.3}$Te electron reflection layer gave PCE 13.4% ($V_{oc}$ 804 mV, $J_{sc}$ 23.1 mA cm$^{-2}$, FF 72%) after annealing at an optimum temperature of 425°C. Te/Cu was deposited on the CdMgTe before Au contacts were deposited.

### 4.5 Nickel telluride and other transition metal tellurides

Nickel telluride (NiTe$_2$) is a semi-metallic material with intrinsic resistivity $10^{-7}$ to $10^{-6}$ Ω cm. It crystallizes with a CdI$_2$-like structure and is stable even with a few percent tellurium deficiency. Although nickel is a well-used contact metal, studies of NiTe$_2$ are less common. Rotlevi et al (2001) and Dobson et al (2002) published studies of electroless NiTe$_2$ contact formation to CdTe. A PCE of ~10% was obtained ($V_{oc}$ ~ 800 mV, $J_{sc}$ ~ 25 mA cm$^{-2}$, FF ~ 65%). Unencapsulated cells were thermally stable to around 200°C, but exposure to water vapor led to reversible degradation.

Other transition metal tellurides have been studied as potential photovoltaic technology materials. There has been little or no experimental work on using them with CdTe absorber solar cells. MoTe$_2$, a layered material, has been numerically modeled as a back contact, but we have not found any experimental data on the work of Dhakal et al (2015) concerning the Mo/CdTe interface and the older work of Lohrer et al (2000) on MBE-grown CdTe/MoTe$_2$ interfaces.

MnTe$_2$, a p-type semiconductor, was tried by Shen et al (2010) as a back contact in substrate configuration devices. MnTe$_2$ was formed on Mo by annealing of Mn/Te bilayers and by direct evaporation of MnTe$_2$. Devices showed severe forward-bias rollover with $V_{oc}$ limited to about 500 mV.

### 4.6 Group IV tellurides

Group IV tellurides are possible materials for back contacts. There are no known experimental studies of silicon telluride (Si$_2$Te$_3$) or germanium telluride back contacts and only one numerical study using AMPS software on CdTe solar cells.

Tin (IV) telluride is a narrow gap semiconductor with a rock-salt structure, which might remain in a zinc-blende structure for very thin layers grown on CdTe. Weng et al (2018) experimented on solar cells with eight different contact structures all including a final 100 nm thick Ni layer. Half of the structures included a light NP etch (intended to remove oxides), and half had a longer NP etch to produce a Te-rich surface. Maximum PCE was obtained with a structure using a light NP etch, 60 nm ZnTe followed by 5 nm of copper then 40 nm SnTe before the metal contact was deposited. This cell gave 14.6% PCE ($V_{oc}$ 841 mV, $J_{sc}$ 24.7 mA cm$^{-2}$, FF 70.2%). T. Shu et al (2019) also used SnTe/Ni back contacts (PCE 13.1%, $V_{oc}$ 782 mV, $J_{sc}$ 24.6 mA cm$^{-2}$, and FF 68%).

Lead telluride (PbTe) has been suggested as a back contact material in 1D simulation studies. XPS has suggested a low VBO between PbTe and CdTe(111) surfaces. It was expected that a two-dimensional electron gas can form at the PbTe/CdTe(111) interface, probably increasing recombination but no experimental solar cell results were available until the work of Swartz et al (2019). They found that despite indications that the CdTe/PbTe:Ti contact was Ohmic, that the PbTe:Ti layer also appeared to be photoconductive. Cells were shunted—limiting the PCE to 9%. The low bandgap of PbTe (~0.29 eV) means that the material is opaque in the NIR and visible bands. Thallium is extremely toxic and not produced in large quantities.
Because Sn and Pb doping in CdTe can cause compensation effects and potential carrier lifetime reduction, it is suggested that research in this area proceed with caution—if sufficient group IV related recombination centers develop over time or with subsequent thermal processing, solar cell performance might be impacted. Group IV and Group V telluride back contact results are summarized in Table 4.

### 4.7 Group V tellurides: arsenic, antimony, and bismuth tellurides

Tellurium does not form a stable compound with nitrogen, and phosphorus telluride bonds are weak. Arsenic (III) telluride, antimony (III) telluride, and bismuth (III) telluride are all stable compounds. Nitrogen, phosphorus, arsenic, and antimony all dope CdTe p-type.

Sb$_2$Te$_3$ is a layered narrow-gap semiconductor with van der Waal's bonding between layers. This forms an intermediate layer. The work function of Sb$_2$Te$_3$ is 5.8 eV, in theory a very good match to p-type CdTe. Sb excess is likely to dope CdTe p-type. Sb$_2$Te$_3$ contacts have been reported twenty years ago (Romeo et al (2000)), Sb$_2$Te$_3$ contacts are reported to produce cells with PCE over 12% (Paudel et al (2011)).

Arsenic telluride (As$_2$Te$_3$) is a narrow gap semiconductor with two crystal phases, monoclinic (most stable at ambient pressure) and rhombohedral. Although not as well studied as a back contact material for CdTe as is Sb$_2$Te$_3$, As$_2$Te$_3$ is likely to dope the interface region of the CdTe with arsenic. Al Turkestani’s As$_2$Te$_3$ contacts outperformed his equivalent Sb$_2$Te$_3$ contacts (PCE 3.6%). Romeo et al (2010) reported 15.8% PCE with As$_2$Te$_3$/Cu contacts—both deposited at 200°C, in this case outperforming Sb$_2$Te$_3$ contacts. Romeo et al (2017) have had higher PCE, finding very similar results (15%-16%, FF 70%-72%) with As$_2$Te$_3$, Bi$_2$Te$_3$, and ZnTe and slightly reduced PCE with Sb$_2$Te$_3$.

It is presumed that the toxicity of arsenic has sometimes driven the preferential choice of Sb$_2$Te$_3$ over As$_2$Te$_3$. When CdTe is heavily doped with arsenic, there is a possibility that some As$_2$Te$_3$ is formed at the rear surface.

Bismuth telluride is a narrow gap semiconductor, with rhombohedral crystal symmetry, that can be doped n-type or p-type. Bismuth is a reasonably cheap and relatively non-toxic element. Lee and Myers (2015) measured a valence band offset of 0.22 eV for the Bi$_2$Te$_3$/CdTe (111) interface. Romeo et al (2013) used Bi$_2$Te$_3$ as a back contact material achieving 10.2% PCE ($V_{oc}$ 775 mV, $J_{sc}$ 22.9 mA cm$^{-2}$, and FF 57.5%).

### 5 Selenium back contacts

Selenides are often chemically like their sulfide counterparts. Many metals form stable selenides. Some of these have a two-dimensional layered structure. The only uses of binary

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**TABLE 3 J-V characteristic parameters for a selection of articles reporting solar cells with ZnTe in the back contact**

<table>
<thead>
<tr>
<th>Reference</th>
<th>back contact</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Process contains Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mondal et al (1992)</td>
<td>ZnTe:Cu</td>
<td>705</td>
<td>18.8</td>
<td>65.7</td>
<td>8.7</td>
<td>Yes</td>
</tr>
<tr>
<td>Mahabaduga et al (2015)</td>
<td>ZnTe:Cu</td>
<td>831</td>
<td>25.5</td>
<td>77.4</td>
<td>16.4</td>
<td>Yes</td>
</tr>
<tr>
<td>J. Li et al (2015)</td>
<td>ZnTe:Cu</td>
<td>852</td>
<td>24.3</td>
<td>73.7</td>
<td>15.3</td>
<td>Yes</td>
</tr>
<tr>
<td>Kindvall et al (2018)</td>
<td>ZnTe:Cu</td>
<td>804</td>
<td>25.8</td>
<td>62</td>
<td>12.89</td>
<td>Yes</td>
</tr>
<tr>
<td>Oklobia et al (2019)</td>
<td>ZnTe:As/Au</td>
<td>696</td>
<td>23.7</td>
<td>72</td>
<td>11.9</td>
<td>No</td>
</tr>
<tr>
<td>Kurley (2016)</td>
<td>Spin-coated ZnTe:Sb</td>
<td>732</td>
<td>16.1</td>
<td>54.0</td>
<td>6.4</td>
<td>No</td>
</tr>
<tr>
<td>Marsillac et al (2007)</td>
<td>ZnTe:N/ITO</td>
<td>550</td>
<td>19.9</td>
<td>52.0</td>
<td>5.7</td>
<td>No</td>
</tr>
<tr>
<td>Makhratchev et al (2000)</td>
<td>ZnTe/ZnTe:N/NI</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>~10</td>
<td>No</td>
</tr>
<tr>
<td>Avachat (2005)</td>
<td>ZnTe:Cu/ITO/Ni-Al</td>
<td>630</td>
<td>7.7</td>
<td>37.9</td>
<td>3.1</td>
<td>Yes</td>
</tr>
<tr>
<td>Ulicna et al (2017)</td>
<td>ZnTe:Cu</td>
<td>727</td>
<td>21.99</td>
<td>70.3</td>
<td>1.25</td>
<td>Yes</td>
</tr>
<tr>
<td>Amin et al (2002)</td>
<td>CdTe/ZnTe/C/Cu/Ag</td>
<td>740</td>
<td>22.98</td>
<td>49</td>
<td>8.31</td>
<td>Yes</td>
</tr>
<tr>
<td>Amin et al (2002)</td>
<td>CdTe/Cd$<em>{0.1}$Zn$</em>{0.9}$Te:N/Au</td>
<td>680</td>
<td>22.6</td>
<td>49</td>
<td>7.46</td>
<td>Yes (?)</td>
</tr>
<tr>
<td>Chen et al (2019)</td>
<td>ITO/ZnO/CdSe/CdTe/ZnTe:Cu</td>
<td>650</td>
<td>19.73</td>
<td>49.75</td>
<td>6.38</td>
<td>Yes</td>
</tr>
</tbody>
</table>
metal selenides as back contacts to CdTe-based solar cells known to the authors are TiSe2 and VSe2. The promising work function value reported by Kraft et al (TSF 2003) for VSe2 did not produce Ohmic contacts when CdTe was deposited on these selenides. This was attributed to the formation of dipoles at the VSe2 to CdTe interface with an excess of Cd present, due to a higher sticking coefficient of Cd.

Zhao (2008) (University of South Florida) attempted to selenize titanium deposited on the back of a CdTe solar cell. However, the high temperatures required for selenization (>420°C) led to deterioration of the CdTe. Later, Ferekides and Morel (2011) reported four candidate metal selenides: TiSe2, VSe2, NbSe2, and TaSe2 (no experimental work). Deposition of TiSe2 onto CdTe by selenization of titanium required too high a processing temperature resulting in some CdTe sublimation.

A possible problem with some transition metal chalcogenide contacts is the existence, in many cases, of multiple phases, often of different stoichiometry. One example is titanium selenide, for which several compounds are reported: Ti9Se2, Ti11Se4 and those listed in Murray (1986).

Studies of a set of a single-metal sulfide, metal selenide, and metal telluride counterparts would be interesting. In the case of selenides, any significant diffusion of Se into CdTe would lead to a reduction in bandgap which might change recombination rates at the rear interface. Selenide back contact solar cell results from the literature are summarized (along with sulfide back contacts) in Table 5. There are no reports of MoSe2 back contacts known to the authors.

### Sulfide Back Contacts

The following metal sulfides are noted as having been used as CdTe back contact materials: CuS, CuInS2, CuInS2:N, CuS/ZnS, FeS2, (Fe,Ni)S2 and MoS2. Other sulfur-containing materials are found listed under other categories (eg, BaCuSF under halides). Sulfide back contact solar cell results from the literature are summarized (with selenide back contacts) in Table 5.

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**Table 4** Selected solar cell J-V parameters from CdTe solar cells with Group IV telluride (SnTe, PbTe) and Group V telluride (As2Te3, Sb2Te3, and Bi2Te3) back contacts reported in the literature

<table>
<thead>
<tr>
<th>Reference</th>
<th>Contact</th>
<th>(V_{oc}) (mV)</th>
<th>(J_{sc}) (mA cm(^{-2}))</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weng et al (2018)(^{15})</td>
<td>ZnTe/Cu/SnTe/metal</td>
<td>841</td>
<td>24.7</td>
<td>70.2</td>
<td>14.6</td>
</tr>
<tr>
<td>Shu et al (2019)(^{96})</td>
<td>SnTe/Ni</td>
<td>782</td>
<td>24.6</td>
<td>68</td>
<td>13.1</td>
</tr>
<tr>
<td>Swartz et al (2019)(^{99})</td>
<td>PbTe:Tl</td>
<td>&lt;700</td>
<td>Unstated</td>
<td>“Shunted”</td>
<td>9</td>
</tr>
<tr>
<td>Romeo et al (1999)(^{242})</td>
<td>Sb2Te3</td>
<td>858</td>
<td>23</td>
<td>74</td>
<td>14.6</td>
</tr>
<tr>
<td>Hodges (2009)(^{473})</td>
<td>Sb2Te3</td>
<td>820</td>
<td>21.3</td>
<td>70.0</td>
<td>12.2</td>
</tr>
<tr>
<td>Hu et al (2011)(^{444})</td>
<td>Sb2Te3</td>
<td>816</td>
<td>25.8</td>
<td>62.3</td>
<td>13.1</td>
</tr>
<tr>
<td>Emziane et al (2005)(^{45})</td>
<td>Sb2Te3/Mo</td>
<td>812</td>
<td>25</td>
<td>69</td>
<td>14</td>
</tr>
<tr>
<td>Paudel et al (2011)(^{108})</td>
<td>Sb2Te3/Cu/Au</td>
<td>778</td>
<td>22.1</td>
<td>71.8</td>
<td>12.3</td>
</tr>
<tr>
<td>Paudel et al (2011)(^{108})</td>
<td>Sb2Te3/Au</td>
<td>717</td>
<td>22.2</td>
<td>63.2</td>
<td>10.1</td>
</tr>
<tr>
<td>Al Turkestani (2007)(^{109})</td>
<td>As2Te3</td>
<td>~600</td>
<td>21.6</td>
<td>41.5</td>
<td>5.4</td>
</tr>
<tr>
<td>Romeo et al (2010)(^{110})</td>
<td>As2Te3/Cu</td>
<td>862</td>
<td>25.5</td>
<td>72</td>
<td>15.8</td>
</tr>
<tr>
<td>Romeo et al (2013)(^{113})</td>
<td>Bi2Te3</td>
<td>775</td>
<td>22.9</td>
<td>57.5</td>
<td>10.2</td>
</tr>
<tr>
<td>Tang et al (2014)(^{114})</td>
<td>Bi2Te3/Ni</td>
<td>650</td>
<td>26.9</td>
<td>60.7</td>
<td>10.6</td>
</tr>
</tbody>
</table>

---

No publications have been found on CdTe solar cells either with NbSe2 or TaSe2 contacts. However, attempts have been made to grow CdTe on NbSe2 substrates. Depositing NbSe2 onto CdTe led to similar dipole formation issues as was reported for VSe2 on CdTe. Gao et al (2014) deposited VSe2 by electron beam evaporation onto CdTe device structures with a copper-free process. The measured J-V curves had a high series resistance but did show an improvement over devices without the VSe2 layer (with VSe2 \(V_{oc}\) 716 mV, \(J_{sc}\) 20.65 mA cm\(^{-2}\) FF 60.5%, and PCE 8.95%).
after annealing at 225°C. Subedi et al (2017)\textsuperscript{127} reported PCE 13% ($V_{oc}$ 806 mV, $J_{sc}$ 22.1 mA cm$^{-2}$, and FF 73%) using (CuS)$_x$(ZnS)$_{1-x}$/Cu/Au back contacts. With copper-containing back contacts, the effect of the back contact is difficult to separate from CdTe doping effects. Woods-Robinson et al.\textsuperscript{128} used a Cu$_{0.60}$Zn$_{0.40}$S back contact to achieve 13.8% PCE ($V_{oc}$ 836 mV, $J_{sc}$ 24.6 mA cm$^{-2}$, and FF 74.4%) using a process that gave 14.0% PCE with a ZnTe:Cu back contact.

Iron sulfide (iron pyrite, FeS$_2$) could be used as a potential back contact in a “Cu-free” process, but iron diffusion into CdTe must be considered. FeS$_2$ nanocrystals, deposited by drop-casting of nanocrystals in a chloroform solution, have been used (Bhandari et al (2015)).\textsuperscript{129-132} as a back contact material. They also compared performance with and without the use of copper. With Cu, a PCE of 13.3% ($V_{oc}$ 810 mV, $J_{sc}$ 21.4 mA cm$^{-2}$, FF 72.8%, series resistance 3.1 $\Omega$ cm$^2$) was achieved. Without Cu, a PCE of 12.5% was achieved. As the energy gap of FeS$_2$ is only 0.95 eV, it will absorb light itself potentially increasing $J_{sc}$, because it is a p-type conductor (not forming an opposing diode). However, the conductivity is low so too thick a layer will add series resistance. (Cu,Fe) S$_2$, tried by Bastola et al (2018)\textsuperscript{133} gave 12% PCE.

Nickel alloyed iron sulfide was used by Bastola et al (2017).\textsuperscript{134} Ni$_{x}$Fe$_{1-x}$S$_2$ was observed to be p-type with up to 10% Ni, but n-type for 20% or greater Ni content. As Ni content increased from 0% to 30%, $V_{oc}$ increased monotonically from 834 to 848 mV, while $J_{sc}$ decreased monotonically (rapidly above 20% Ni). FF reached a maximum at 5% Ni, as did efficiency (PCE 11.8%, $V_{oc}$ 835 mV, $J_{sc}$ 19.7 mA cm$^{-2}$, and FF 70.8%). The Ni$_{0.05}$Fe$_{0.95}$S$_2$/Au contact was a small (8% relative) improvement on their standard Cu/Au contact.

Nickel sulfide has been tried as a hole transport layer in perovskites\textsuperscript{135} (Ni$_2$S composite with carbon gave low-performance perovskite solar cells with PCE ~5%, $V_{oc}$ < 600 mV, FF < 40%), but no reports have been found using Ni$_2$S in CdTe solar cells.

Barium copper sulfide (BaCu$_2$S$_3$ or BCS) has been used by Subedi et al (2019)\textsuperscript{136} in a recent bifacial solar cell study, in which ITO was deposited on top of ~100 nm of BCS on 3 $\mu$m of CdTe. Front-side (through glass) illumination gave PCE 12.3% ($V_{oc}$ 823 mV, $J_{sc}$ 21.2 mA cm$^{-2}$, FF 70.4%, and $R_s$ 3.8 $\Omega$ cm$^2$), but only a PCE of 1% when rear illuminated ($J_{sc}$ 2.8 mA cm$^{-2}$).

In the substrate configuration, X. Tan (2017)\textsuperscript{137} at the University of Toledo has studied CIS and nitrogen-doped CIS as back contacts in glass/Mo/CIS/CdTe/CdS solar cells. The best PCE was only 3.8% in a variant structure (glass/Mo/MoO$_x$/CIS:N/CdTe/CdS).

Molybdenum sulfide (MoS$_2$) was used as a back contact material by Yuan et al (2017).\textsuperscript{138} A study of different thicknesses of MoS$_2$ gave a maximum PCE of 13.7%. The estimated valence band offset between CdTe and MoS$_2$ was 0.56 eV, whereas Deng et al (2020)\textsuperscript{139} estimated 0.46 eV. The contact metal used by Yuan et al was gold (good work function match to MoS$_2$); nickel would have been an interesting comparison. It is noted that making Ohmic contacts to MoS$_2$ is itself not trivial.\textsuperscript{140}

## 7 Metal Oxide Back Contacts

Oxides are often used as transparent conducting front contact materials (eg, SnO$_2$:In (ITO), SnO$_2$:F (FTO), ZnO:Al (AZO)). Bandgap values are mostly larger than their sulfide, selenide, and telluride counterparts. As the properties of individual oxides vary considerably, it is better to discuss each oxide separately. However, an attempt is made to group 3d transition metal oxides, where there are some similarities such as the possibility of mixed valency of the metal in the case of molybdenum and vanadium oxides. Diffusion of 3d metal ions into CdTe must be considered, especially for those cases in which deep levels are formed which can in some cases dramatically decrease minority carrier lifetime.

The question of what role the oxygen plays at CdTe surfaces, interfaces, and grain boundaries is interesting. Air or oxygen anneals before metallization have been found to improve device performance in arsenic-doped CdTe\textsuperscript{141} and some Cu-doped processes. Major (2016)\textsuperscript{142} discussed the effect of oxygen on grain boundaries largely, but not completely, from the point of view of oxygen exposure during CdTe growth or the CdCl$_2$ activation process.

### 7.1 Zinc oxide

Zinc (II) oxide (ZnO) is a wide-gap semiconductor with a wurzite crystal structure and an ambient temperature bandgap of around 3.3 eV. ZnO heavily doped with aluminum (AZO) is a well-known transparent conducting oxide (TCO), and has been used both as a front contact,\textsuperscript{143} and as a back contact material (Parikh (2007),\textsuperscript{144} Heisler et al (2013)\textsuperscript{145}) for CdTe absorber solar cells. Aluminum doping greatly increases the conductivity of ZnO and introduces a Moss-Burstein shift of the bandgap to higher photon energy.

Parikh,\textsuperscript{144} using a thin 80 nm thickness of ZnO:Al obtained 1.79% PCE with no copper, and 5.74% PCE ($V_{oc}$ 475 mV, $J_{sc}$ 22.9 mA cm$^{-2}$, and FF 52.7%) with the use of copper before ZnO:Al deposition (and a short 150°C anneal). Heisler et al (2013)\textsuperscript{145} used RF sputtered ZnO:Al back contacts with both 0.7 and 1.7 $\mu$m thick CdTe absorbers, obtaining a maximum PCE of 8.6% (best cell: $V_{oc}$ 744 mV, $J_{sc}$ 19.4 mA cm$^{-2}$, and FF 60%) for the thicker CdTe.

Duenow et al (2009)\textsuperscript{146} published data on composite ZnTe:Cu/ZnO:Al back contacted CdTe cells (also ZnTe:Cu/
ITO back contacts), obtaining 10.2% PCE (Voc 798 mV, Jsc 20.7 mA cm\(^{-2}\), and FF 61.7%).

### 7.2 Indium oxides

Indium-doped tin oxide (ITO), a highly conductive n-type TCO, has been used as a back contact material. The use of ITO as a back contact interface material is not intuitive as ITO/CdTe junctions have been used as solar cells diode junctions.

Calnan (2008)\(^{147}\) looked at the optical transmission of indium-doped metal oxides for front and back contacts to CdTe absorber cells\(^{148}\), but did not publish any CdTe absorber solar cell PCE data.

Romeo et. (2007)\(^{149}\) obtained 10% PCE with a Cu/ITO back contact, 8in a cell which was bifacial. Using nanocrystal CdTe in an ink, Crisp et al (2014)\(^{150}\) obtained PCE 11.3% (Voc 686 mV, Jsc 25.5 mA cm\(^{-2}\), FF 64.7%) with a ZnO/CdTe/ITO device in which the n-p junction was between the ZnO and CdTe and ITO formed the back contact. Swartz et al (2019)\(^{99}\) using an ITO/Au back contact on a CdTe nanoparticle treated CdTe absorber obtained PCE 14.7% with other J-V parameters not explicitly stated.

### 7.3 Molybdenum oxide

Molybdenum (VI) oxide (MoO\(_3\)-\(_x\)) is a wide bandgap semiconductor,\(^{151}\) which when perfectly stoichiometric, has a layered structure. As oxygen is lost from MoO\(_3\), the bandgap narrows, the material increases in conductivity, and the material structure becomes more complex. Metallic molybdenum (IV) oxide (MoO\(_2\)) can be formed from MoO\(_3\) in reducing conditions.\(^{152,153}\)

Table 6 lists several of the papers to publish results using MoO\(_3\)-\(_x\) as a back contact for CdTe absorber solar cells. Most of these results are on superstrate configuration cells, except where noted below. It can be seen from Table 6 that several different metals have been used on top of the MoO\(_x\), this additional step adds a further complexity to the back contact and reduces the ability to directly compare results from the different groups. The top PCE reported for a MoO\(_x\) back contact is 14.6% for a process which includes the use of copper\(^{154}\) and 14.1% for a process which excludes copper.\(^{155}\)

H. Lin (2012)\(^{156}\) observed some Mo\(^{5+}\) formation when sputtering, but not when thermally evaporating molybdenum oxide. The minimum series resistance obtained was 4.7 Ω cm\(^2\) with 40 nm of evaporated MoO\(_3\)-\(_x\) and nickel metallization. An advantage of the MoO\(_3\)-\(_x\) layer is that several low-cost metals (including aluminum) can be used on the MoO\(_3\)-\(_x\) surface; expensive, high work function metals are not necessary. However, the highest Voc achieved by any researchers found in this analysis was using a gold metallization.\(^{157}\) Lin et al\(^{155}\) showed greater PCE stability of CdTe devices when using Ni or Mo metallization on MoO\(_3\) at the back contact compared to the less stable Cr and Mg metals, and a very unstable Al contact. The stability tests used were a 19 hours anneal at 200°C and a 400 day light-soak.

Paudel and Yan (2014)\(^{158}\) performed x-ray photoelectron spectroscopy measurements on the CdTe to MoO\(_3\) interface finding a 2.75 ± 0.2 eV valence band offset (barrier to holes). Their FF decreased with increasing MoO\(_3\) thickness from 2 nm.

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**Table 5** J-V parameters of CdTe solar cells with selenide and sulfide materials as back contactS

<table>
<thead>
<tr>
<th>Reference back contact material</th>
<th>Voc (mV)</th>
<th>Jsc (mA cm(^{-2}))</th>
<th>FF (%)</th>
<th>Rs (Ω cm(^2))</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gao et al (2014)(^{120}) VSe(_2)</td>
<td>716</td>
<td>20.65</td>
<td>60.5</td>
<td>131</td>
<td>8.95</td>
</tr>
<tr>
<td>Kim et al (2003)(^{124}) CuS</td>
<td>840</td>
<td>19.45</td>
<td>69.6</td>
<td>-</td>
<td>11.37</td>
</tr>
<tr>
<td>Türck et al (2015)(^{126}) CuS</td>
<td>~800</td>
<td>~24</td>
<td>~70</td>
<td>-</td>
<td>13</td>
</tr>
<tr>
<td>Zhang et al (2016)(^{126}) Cu(_2)S(_3)</td>
<td>797</td>
<td>24.00</td>
<td>72.1</td>
<td>-</td>
<td>13.8</td>
</tr>
<tr>
<td>Lei et al (2013)(^{125}) Cu, S/Ni</td>
<td>820</td>
<td>21.60</td>
<td>68.9</td>
<td>-</td>
<td>12.2</td>
</tr>
<tr>
<td>Bhandari et al (2015)(^{129}) FeS(_2)/Au (1 µm/30 nm) (no Cu)</td>
<td>811</td>
<td>23.00</td>
<td>67.0</td>
<td>-</td>
<td>12.5</td>
</tr>
<tr>
<td>Bhandari et al (2017)(^{130}) FeS(_2) (with Cu)</td>
<td>810</td>
<td>21.40</td>
<td>72.8</td>
<td>3.1</td>
<td>13.3</td>
</tr>
<tr>
<td>Bastola et al (2017)(^{134}) (Fe(<em>{0.95})Ni(</em>{0.05}))S(_2) (with Cu)</td>
<td>835</td>
<td>19.70</td>
<td>70.8</td>
<td>-</td>
<td>11.8</td>
</tr>
<tr>
<td>Rockett et al (2018)(^{247}) FeS(_2)/Au</td>
<td>811</td>
<td>23.00</td>
<td>68.9</td>
<td>~6</td>
<td>12.5</td>
</tr>
<tr>
<td>Rockett et al (2018)(^{247}) CuFeS(_2)/Au</td>
<td>803</td>
<td>22.50</td>
<td>70.9</td>
<td>-</td>
<td>12.8</td>
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<tr>
<td>Bastola et al (2018)(^{133}) Cu/CuFeS(_2)/Au</td>
<td>823</td>
<td>19.20</td>
<td>74.6</td>
<td>3.3</td>
<td>12</td>
</tr>
<tr>
<td>Yuan et al (2017)(^{138}) Cu/MoS(_2)/Au</td>
<td>752</td>
<td>25.90</td>
<td>70.0</td>
<td>-</td>
<td>13.7</td>
</tr>
<tr>
<td>Woods-Robinson et al.(^{128}) CuZnS</td>
<td>836</td>
<td>14.60</td>
<td>74.4</td>
<td>3.9</td>
<td>13.8</td>
</tr>
</tbody>
</table>

Note: Series resistance (Rs) is given when found within the reference.
to 40 nm (series resistance increased). An increase in $V_{oc}$ by 50 mV was observed when a 2 nm thick MoO$_3$ layer was used. Gretener (2015), using substrate configuration cells, concluded that MoO$_2$ was present at the CdTe interface in the highest performing cells. MoO$_2$ is expected to have a higher work function and more metallic conduction than MoO$_3$. Drayton (2015) also found that low-temperature deposition MoO$_x$ deposition gave MoO$_2$ XPS peak positions.

Ta$_2$O$_5$ has been successfully used as a high resistance layer between CdS and CdTe (increasing $V_{oc}$ and FF), but no results have been found using Ta$_2$O$_5$ as a back contact interfacial layer.

### 7.4 3d transition metal oxides

Vanadium oxide and nickel oxide have been used as CdTe absorber solar cell back contact materials. Transition metals from the 3d series often form deep levels within semiconductors. If CdTe carrier lifetime is reduced by the 3d transition metal, and there is a mechanism for diffusion, then that metal oxide is probably best avoided.

Vanadium can form the following oxides: V$_2$O$_3$, VO$_2$, and V$_2$O$_5$. The bandgaps of the vanadium (III) and vanadium (IV) oxides are narrow, only the vanadium (V) oxide bandgap is wide enough to be useful as a front contact, or as a back contact with high transmission in the visible or NIR. Deposited V$_2$O$_5$ films can have a range of bandgaps from 2.25 to 3.1 eV. V$_2$O$_5$ is thermochromic that its color (bandgap) changes rapidly (decreases) with increasing temperature. Vanadium doping of CdTe can produce associated deep levels and is used to produce very resistive CdTe.

Paudel et al (2015) looked at three transition metal oxides (MoO$_{3-x}$, V$_2$O$_{5-x}$, and WO$_{3-x}$) with a view to making copper-free back contacts. Within these three systems, the best PCE was using molybdenum oxide ($14.1\%$ PCE, $V_{oc}$ 815 mV, $J_{sc}$ 25.1 mA cm$^{-2}$, FF 66.7%, and $R_s$ 6.5 $\Omega$ cm$^2$), whereas the vanadium oxide cells gave $13.6\%$ ($V_{oc}$ 778 mV, $J_{sc}$ 25.1 mA cm$^{-2}$, FF 69.4%, and $R_s$ 6.2 $\Omega$ cm$^2$), and the tungsten oxide $12.9\%$ ($V_{oc}$ 767 mV, $J_{sc}$ 24.6 mA cm$^{-2}$, FF 66.7%, and $R_s$ 6.5 $\Omega$ cm$^2$).

Shen et al (2016) obtained $10.4\%$ PCE ($V_{oc}$ 729 mV, $J_{sc}$ 24.7 mA cm$^{-2}$, and FF 57.6%) using gold contacts to V$_2$O$_5$ back contacts. These results were further improved using a thin (2 nm) Cu layer before the V$_2$O$_5$ deposition leading to $13.7\%$ PCE ($V_{oc}$ 797 mV, $J_{sc}$ 24.8 mA cm$^{-2}$, and FF 69.4%), very similar to Paudel el. (2015). On timescales of up to a year, some PCE degradation was observed due to a small increase in series resistance.

Nickel (II) oxide (NiO), a p-type semiconductor, was used as a CdTe back contact by Ishikawa et al (2016) and Xiao et al (2017). Ishikawa et al used sputtered Ag-doped NiO back contacts. PCE with NiO:Ag was $5.14\%$ ($V_{oc}$ 598 mV, $J_{sc}$ 16.4 mA cm$^{-2}$, and FF 53%), compared to a baseline carbon-based contact giving PCE $15.3\%$. In the work of Xiao et al PCE was maximized at 20 nm NiO thickness and further improved with a 3 nm thick layer of copper deposited before.

### TABLE 6

<table>
<thead>
<tr>
<th>Reference</th>
<th>Device structure or contact</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Process contains copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yang et al (2016)</td>
<td>CdTe/Cu/MoO$_x$/Cu-Au</td>
<td>799</td>
<td>25.3</td>
<td>70.1</td>
<td>14.2</td>
<td>Yes</td>
</tr>
<tr>
<td>Zhang et al (2018)</td>
<td>CdTe/MoO$_x$/Cu</td>
<td>830</td>
<td>24.2</td>
<td>72.7</td>
<td>14.6</td>
<td>Yes</td>
</tr>
<tr>
<td>Wang et al (2018)</td>
<td>CdTe/MoO$_x$/Mo</td>
<td>794</td>
<td>24.9</td>
<td>69.0</td>
<td>13.7</td>
<td>Yes</td>
</tr>
<tr>
<td>Hao Lin et al (2012)</td>
<td>CdTe/MoO$_x$/Ni</td>
<td>808</td>
<td>22.0</td>
<td>72.6</td>
<td>12.9</td>
<td>No</td>
</tr>
<tr>
<td>Hao Lin et al (2012)</td>
<td>CdTe/MoO$_x$/Al (superstrate)</td>
<td>815</td>
<td>22.3</td>
<td>68.4</td>
<td>12.4</td>
<td>No</td>
</tr>
<tr>
<td>Drayton et al (2015)</td>
<td>Cu/MoO$_x$/Ni</td>
<td>792</td>
<td>21.9</td>
<td>68.3</td>
<td>11.9</td>
<td>Yes</td>
</tr>
<tr>
<td>Paudel et al (2015)</td>
<td>MoO$_x$/Au</td>
<td>790</td>
<td>22.6</td>
<td>65.0</td>
<td>11.6</td>
<td>No</td>
</tr>
<tr>
<td>Perrenoud (2012)</td>
<td>Te/MoO$_x$/Cu</td>
<td>833</td>
<td>22.4</td>
<td>71.4</td>
<td>13.3</td>
<td>Yes</td>
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<tr>
<td>Irfan et al (2012)</td>
<td>MoO$_x$/Ni</td>
<td>807</td>
<td>20.7</td>
<td>70.8</td>
<td>11.8</td>
<td>Uncertain</td>
</tr>
<tr>
<td>Perrenoud (2012)</td>
<td>Cu/Te/MoO$_x$</td>
<td>768</td>
<td>21.4</td>
<td>68.6</td>
<td>11.3</td>
<td>Yes</td>
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<tr>
<td>Greterener (2015)</td>
<td>MoO$_x$/Te/CdTe (substrate)</td>
<td>733</td>
<td>22.0</td>
<td>62.3</td>
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<td>Yes</td>
</tr>
<tr>
<td>Greterener (2015)</td>
<td>MoO$_x$/CdTe</td>
<td>597</td>
<td>20.3</td>
<td>48.4</td>
<td>5.9</td>
<td>Yes</td>
</tr>
<tr>
<td>Dang and Singh (2015)</td>
<td>Substrate/NW CdS/CdTe/MoO$_3$/Au</td>
<td>752</td>
<td>25.6</td>
<td>57.1</td>
<td>11.0</td>
<td>No</td>
</tr>
<tr>
<td>Artegiani (2019)</td>
<td>CdTe/MoO$_x$/Au</td>
<td>852</td>
<td>19.4</td>
<td>61.6</td>
<td>10.2</td>
<td>Yes</td>
</tr>
</tbody>
</table>
the NiO. Maximum PCE with the Cu layer was 13.5% ($V_{oc}$ 791 mV, $J_{sc}$ 23.7 mA cm$^{-2}$, FF 68.9%, and $R$ 9.5 Ω cm$^{-2}$); without Cu, the maximum PCE was 12.2% (rollover in forward bias). Degradation in PCE at 80°C was reduced with 20 nm NiO in the back contact.

Alloying nickel oxide with cobalt ($Ni_{1-x}Co_xO_2$) is a possibility for fine tuning of the material's electron affinity (probably at the expense of conductivity).

Titanium dioxide ($TiO_2$) is widely used as an electrode material in organic solar cells. However, it has not been tried (to the authors' knowledge) as a CdTe solar cell back contact material probably due to its expected high valence band offset (2.6 eV$^{158}$). TiO$_2$ has been used as an n-type buffer layer$^{169}$ for p-CdTe absorber solar cells. Titanium metal has been used as a back contact (NREL 2009).$^{146}$ Oxide formation over time could lead to a possible TiO$_2$ intermediate layer. Long-term diffusion of Ti into CdTe might reduce doping levels due to deep level formation.$^{170}$

No other 3d transition metal oxides are known to have been used as CdTe absorber cell back contact materials.

### 7.5 | Aluminum oxide

Very thin layers of aluminum oxide ($Al_2O_3$) have been suggested as passivation layers for the rear surface of CdTe. $Al_2O_3$ has a very large bandgap and is typically very insulating. An $Al_2O_3$ barrier must be very thin to enable electrons to tunnel through. For very thin layers, there is the issue of uniformity, do areas exist with missing $Al_2O_3$ or thicker regions exist where tunneling is inhibited? This is a difficult characterization issue at a buried interface that is also typically very rough.

The motivation for this approach is that minority carrier lifetimes have been observed to increase in some semiconductor systems when $Al_2O_3$ is applied to the surface (eg, HgCdTe,$^{171}$ Si,$^{172}$ and CIGS$^{173}$). However, in a solar cell, the interface must pass current and impressive increases in lifetime in $Al_2O_3$ passivated CdTe$^{174}$ have not been developed into cells with excellent PCE.

There is also the question of whether copper is used in the process, so the interface in some studies can be to other materials (eg, CdTe/Cu$_x$Te/Al$_2O_3$)$^{175}$, rather than directly depositing $Al_2O_3$ onto CdTe.

Atomic layer deposited (ALD) $Al_2O_3$ on TECTM 10 substrates has also been used to overcome shorts due to pinholes in CdTe solar cells (TECTM 10/Al$_2O_3$/CdS/CdTe/ZnTe/Cu/ Ni).$^{176}$ Liang et al (2015)$^{177}$ obtained PCE 12.1% using 1 nm thick ALD $Al_2O_3$. Lin et al (2016)$^{178}$ achieved PCE of 13.0% ($V_{oc}$ 782 mV, $J_{sc}$ 24.2 mA cm$^{-2}$, and FF 68%) with a 9 nm Cu back contact layer followed by a 2 nm ALD-$Al_2O_3$ layer. Munshi et al (2018)$^{179}$ achieved PCE 16.5% ($V_{oc}$ 827 mV, $J_{sc}$ 28.1 mA cm$^{-2}$, and FF 71.1%) with a thin 0.5 nm $Al_2O_3$ layer, but this was with dual Cd(Se,Te)/CdTe absorber layers which gave slightly higher $V_{oc}$ and FF (same $J_{sc}$) without the $Al_2O_3$ layer.

### 7.6 | Copper oxide

There are three stoichiometric copper oxide compounds ($Cu_2O$, CuO, and $Cu_3O_4$).$^{180}$ Copper (I) oxide ($Cu_2O$) is a p-type semiconductor with a bandgap of ~2.1 eV. The contact resistance of $Cu_2O$ on p-type CdTe was measured by Ghosh et al (2002).$^{181}$ The contact resistance measurement of 2.2 × $10^{-2}$ Ω cm$^{-2}$ appeared favorable compared to similar measurements the authors performed on Ni-P/Au, Cu/Au, or Sb/Au contacts. Türck et al (2016)$^{182}$ obtained PCE 15.2% ($V_{oc}$ 832 mV, $J_{sc}$ 25.0 mA cm$^{-2}$, and FF 73.1%) on a CdTe absorber cell on TECTM 15M substrate with CdS:O buffer and a Cu$_2$O/Au back contact. Heat treatment was required after Cu$_2$O deposition to achieve high PCE. Masood et al (2017)$^{183}$ at the University of Science and Technology of China, Hefei estimated the barrier height at the CuO/CdTe interface to be around 0.35-0.44 eV. Their best PCE was 12.2% ($V_{oc}$ 753mV, $J_{sc}$ 26.7 mA cm$^{-2}$, and FF 60.2%) with 10 nm CuO deposited before gold metallization. Cu$_2$O has also been used as a HTM in perovskite solar cells,$^{184}$ and its electronic properties compared with other copper compounds.$^{15}$

### 7.7 | Oxide back contacts compared

Table 7 shows a comparison of the highest PCE CdTe absorber solar cells found in the literature using different oxide back contact materials. The maximum $V_{oc}$ with an oxide back contact is about 830 mV—this is 20-40 mV below the maximum $V_{oc}$ routinely achieved in several laboratories in recent years. $J_{sc}$ is more difficult to compare between different laboratories, but with five reports of oxide materials greater than 24 mA cm$^{-2}$ some oxides can certainly pass significant current at zero bias. No FF above 73.1% has been achieved with an oxide back contact.

It would be interesting to see more oxide materials applied to graded Cd(Se,Te) absorber solar cells.

### 8 | Metal pnictide back contacts

Metal pnictides have been little used as back contacts. Two examples of CdTe back contacts using single-metal nitrides have been found: ZrN (PCE 1.68% in 2014$^{185}$) and MoN$_x$ (Guntur (2011$^{186}$), Drayton et al (2015)$^{159}$ (PCE 5.24%). A more recent article (Kindvall et al (2017)$^{187}$) on the use of MoN$_x$ (and MoO$_x$) on substrate configuration cells did not
explicitly state PCE values but did contain numerous J-V parameters presented in graphic form. When a thick MoN film was used as a back contact, the J-V curves appeared very similar (PCE 12.3%, $V_{oc} \sim 780-800$ mV, $J_{sc} \sim 23$ mA cm$^{-2}$, FF \sim 70%, estimated from graphs) to their control device (Te then Ni based paint).

ZrN has been used as a CIGS back contact—optically reflective but with increased series resistance and interface recombination. MoN has been used as a diffusion barrier in CIGS solar cells. Nickel phosphide was considered as a back contact material. In this case, Ni$_2$P powder was mixed with the graphite paste applied to the back contact.

The use of p-nictides within CdTe absorber solar cell back contact structures is not particularly mature, and no advantage over more established back contact technologies has yet been achieved.

### 9 | INORGANIC BACK CONTACTS CONTAINING HALIDES

Some complex fluorides have been suggested as p-type transparent contact materials. Spies (2007) at Oregon State University examined the use of barium copper tellurium fluoride (BCTF, bandgap 2.3 eV, hole concentration of $10^{20}$-$10^{21}$ cm$^{-3}$, mobility 1-5 cm$^2$ V$^{-1}$ s$^{-1}$) as a CdTe absorber solar cell back contact. A PCE of 1.2% was obtained ($V_{oc}$ 540 mV, $J_{sc}$ 4.8 mA cm$^{-2}$, and FF 46%).

A collaboration in Japan between Ryukoku University and the Kisanarai National College of Technology, Chiba, has studied PLD quaternary chalcogenide fluoride materials for back contacts. Their first paper (2014) used the selenide-fluoride BaCuSeF. A PCE of 2.82% ($V_{oc}$ 796 mV, $J_{sc}$ 6.0 mA cm$^{-2}$, and FF 59%) was obtained, which increased to 3.18% ($V_{oc}$ 714 mV, $J_{sc}$ 9.21 mA cm$^{-2}$, and FF 41%) with the inclusion of a thin Ni$_{0.97}$Li$_{0.03}$O interlayer. PCE was improved with a bromine-based back-surface treatment (PCE 9.91%, $V_{oc}$ 805 mV, $J_{sc}$ 22.1 mA cm$^{-2}$, and FF 55.7%). It is noted that a Cu$_2$Te layer formed during processing with x \sim 1.4. Using strontium instead of barium and improving back-surface conductance by using ITO on top of the fluoride layer improved the PCE to 14.3% ($V_{oc}$ 804 mV, $J_{sc}$ 27.5 mA cm$^{-2}$—very high if reproducible, FF 65%). The optimum thickness of SrCuSeF was 34 nm (with 200 nm of ITO on top). The authors believe that the low conductivity of the fluoride layer is limiting series resistance and hence FF. Doping with sodium gave a small improvement in FF raising the PCE to 14.7% ($V_{oc}$ 806 mV, $J_{sc}$ 27.5 mA cm$^{-2}$, and FF 66.1%). Substituting sulfur for selenium (BaCuSF), again used with ITO on top (platinum metallization), gave PCE 13.9% ($V_{oc}$ 818 mV, $J_{sc}$ 25.2 mA cm$^{-2}$, and FF 67.5%).

The use of quaternary inorganic materials allows a huge range of potential materials to be considered. However, controlling the composition of many quaternary materials can often be difficult compared to ternary or binary materials, as well as allowing a large range of potential native defects.

Perovskite halide back contacts to CdTe devices have been studied by the University of Toledo group. Small performance gains (4-9 mV in $V_{oc}$, 1.4%-2.1% in absolute FF) were achieved over their standard Cu/Au back contacts. Some devices gave $V_{oc}$ 870 mV which the authors said they would investigate further. The authors also have used the reaction of methylammonium iodide (MAI) with cadmium iodide (forming (CH$_3$NH$_3$)$_2$CdI$_4$ or MA$_2$CdI$_4$) perovskite in solution) to selectively remove Cd from the back surface, leaving the surface Te-rich. Either copper/gold or ITO contacts (transparent) were then applied. MAI treated CdTe with Cu/Au contacts achieved 13.0% average PCE ($V_{oc}$ 824 mV, $J_{sc}$ 20.5 mA cm$^{-2}$, and FF 77.1%) and 13.5% in the champion cell. MAI treated CdTe with Cu/ITO back contacts achieved 12.2% ($V_{oc}$ 823 mV, $J_{sc}$ 21.4 mA cm$^{-2}$, and FF 69.3%); MAI treated CdTe with Cu-free ITO back contacts gave a champion cell with PCE 10.0% ($V_{oc}$ 748 mV, $J_{sc}$ 21.0 mA cm$^{-2}$, and FF 57.9%). The Cu-free cell therefore had reduced $V_{oc}$ and FF.

### Table 7 Comparison of best CdTe absorber solar cell performance with different oxide back contacts

<table>
<thead>
<tr>
<th>Reference</th>
<th>Oxide back contact</th>
<th>$V_{oc}$ of maximum PCE cell (mV)</th>
<th>$J_{sc}$ of maximum PCE cell (mA cm$^{-2}$)</th>
<th>FF of maximum PCE cell (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Türck et al (2016)</td>
<td>Cu$_2$O</td>
<td>832</td>
<td>25.0</td>
<td>73.1</td>
<td>15.2</td>
</tr>
<tr>
<td>Zhang et al (2018)</td>
<td>CdTe/MoO$_3$/Cu</td>
<td>830</td>
<td>24.2</td>
<td>82.7</td>
<td>14.6</td>
</tr>
<tr>
<td>Shen et al (2016)</td>
<td>V$_2$O$_5$</td>
<td>806</td>
<td>24.8</td>
<td>70.0</td>
<td>14.0</td>
</tr>
<tr>
<td>Paudel et al (2013)</td>
<td>WO$_3$</td>
<td>787</td>
<td>24.6</td>
<td>66.7</td>
<td>12.9</td>
</tr>
<tr>
<td>Xiao et al (2017)</td>
<td>Cu/InO</td>
<td>796</td>
<td>24.2</td>
<td>70.2</td>
<td>13.5</td>
</tr>
<tr>
<td>Heisler et al (2013)</td>
<td>ZnO:Al</td>
<td>745</td>
<td>19.3</td>
<td>64</td>
<td>9.3</td>
</tr>
<tr>
<td>Khrypunov et al (2019)</td>
<td>ITO</td>
<td>808</td>
<td>18.7</td>
<td>69</td>
<td>10.4</td>
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<tr>
<td>Swartz et al (2019)</td>
<td>ITO/Au</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>14.7</td>
</tr>
</tbody>
</table>
Copper (I) iodide has been used as a back contact material (Li et al. (2019))\textsuperscript{208}. PCE was maximized with a very thin (5 nm) CuI layer (PCE 14.5%, $V_{oc}$ 795 mV, $J_{sc}$ 25.4 mA cm$^{-2}$, FF 71.9%, and $R_s$ 3.6 $\Omega$ cm$^2$). CuI has also been used as a perovskite HTM.\textsuperscript{15} Copper (II) chloride has been used by Artegiani et al. (2019).\textsuperscript{201} In this case, the copper halide is thought to be acting as a reproducible source for a very small amount of copper (equivalent to 0.1 nm of pure copper) leading to an improvement in device stability after 1000 hours of 80°C stress testing.

Copper is common to all the halide-based back contact technologies listed in Table 8; of the back contact materials in Table 8, only perovskites are potentially compatible with a Cu-free process.

10 | INORGANIC CARBON-BASED BACK CONTACTS

In this section, carbon allotrope back contacts and some materials containing carbon atoms are examined. Several forms of carbon have been used as back contacts, perhaps reflecting the wider research of the time on an allotrope. Graphite is a low-cost material which can be formed easily into a cheap paste, which is often convenient for small laboratories. Such pastes can also be loaded with metal particles, such as copper or silver, or as mentioned earlier HgTe.

The use of graphene with thin film solar cells including CdTe has been reviewed recently (Shi and Jayatissa (2018))\textsuperscript{202}; this included the usage of graphene in the front contact. Cu nanowires combined with graphene were used by Liang et al. (2012)\textsuperscript{203} (PCE 12.1%, $V_{oc}$ 801 mV, $J_{sc}$ 22.4 mA cm$^{-2}$, and FF 67.4%); this could be just a reasonably effective way of delivering restricted amounts of copper to the back surface. Graphene has been studied, doped with boron by Lin et al. (2011)\textsuperscript{204} (PCE 7.86%, $V_{oc}$ 674 mV, $J_{sc}$ 22.0 mA cm$^{-2}$, and FF 55.2%).

Single-Walled carbon nanotubes (SWCNT) have also been used. Barnes et al. (2007)\textsuperscript{205} used SWCNTs as a transparent back contact on top of CuTe on CdTe (PCE 12.4%). Khanal’s Cu-free SWCNT device\textsuperscript{206} reached 11.3% PCE ($V_{oc}$ 788 mV, $J_{sc}$ 21.8 mA cm$^{-2}$, and FF 66.5%). Phillips et al. (2013)\textsuperscript{22} reported further work on SWCNT/Au contacts, reporting 11.0 ± 2.8% PCE. Bin Li et al. (2016)\textsuperscript{207} obtained 9.71% PCE ($V_{oc}$ 692 mV, $J_{sc}$ 22.7 mA cm$^{-2}$, and FF 61.9%) after a 320°C annealing step. Alfadhili et al. (2017)\textsuperscript{208} attempted to dope SWCNTs with triethylwoloxonium hexachlorantimonate increasing $V_{oc}$ but adversely impacting FF (best results: PCE 10.6%, $V_{oc}$ 805 mV, $J_{sc}$ 19.4 mA cm$^{-2}$, and FF 68.9%).

The mobility of individual nanotubes is very high, up to 10$^5$ cm$^2$ V$^{-1}$ s$^{-1}$, but the effective sheet resistance remains high compared to good TCOs, at over 500 $\Omega$/sq at a film thickness of 500 nm, due to relatively poor conduction between nanotubes. This is a generic issue with nanowire structures in any material for use as a carrier transport layer in solar cells: both internal conductivity and effective contact conductance need to be high.

Koirala et al. (2014)\textsuperscript{209} studied PECVD grown silicon alloyed with carbon, heavily p-type doped with hydrogen and boron (a-Si$_{1-x}$C$_x$:H) as a CdTe back contact material. The devices had a high series resistance (12 $\Omega$ cm$^2$), reducing FF (48.8%) compared to their reference Cu/Au contacts (FF 67%).

Considering carbon containing compounds, Paudel and Yan (2016)\textsuperscript{210} tried copper thiocyanate (CuSCN) back contacts. This was not the first use of CuSCN as a back contact as Tenazaera et al. (2005)\textsuperscript{211} had used it in a thin absorber solar cell of structure ZnO/CdTe/CuSCN, obtaining very poor preliminary solar cell J-V parameters ($V_{oc}$ ~ 200 mV, $J_{sc}$ < 1 mA cm$^{-2}$, and FF 28%). A high PCE of 13.7% was obtained ($V_{oc}$ 866 mV, $J_{sc}$ 22.9 mA cm$^{-2}$, and FF 69.1%, $R_s$ 6.6 $\Omega$ cm$^2$) with a 5 nm thick CuSCN layer. CuSCN, a wide bandgap (3.4-3.9 eV) p-type semiconductor,\textsuperscript{212} has been used successfully as a HTM with perovskites, reportedly improving their thermal stability compared to many organic HTMs,\textsuperscript{213} and acting as a passivating agent for unbonded lead. Similar CdTe solar cell PCE values were obtained by Pressman (2017)\textsuperscript{214} at the University of Liverpool (PCE 13%, $V_{oc}$ 780 mV, and $J_{sc}$ 26 mA cm$^{-2}$).

Montgomery et al. (2019)\textsuperscript{215} (University of Alabama) used two different solvents to deposit CuSCN on the back of a CdSe-CdTe solar cell obtaining 17% PCE, using a CdSe buffer the results are not entirely comparable to CdS buffer cells, but the $V_{oc}$ and FF are very good. Forward-bias rollover is suppressed with CuSCN contacts. It is difficult to deconvolve the thiocyanate intermediate layer from copper doping effects. AgSCN has also been used by the Alabama group (Yan et al. (2019))\textsuperscript{216}.

Selected experimental solar cell parameter results from the literature for carbon containing inorganic contacts are collected in Table 9.

11 | ORGANIC MATERIALS AS BACK CONTACTS

Organic contacts can provide interlayers on CdTe. Several materials have been tried, mostly HTMs that have been commonly used before in polymer, DSSC, and perovskite solar cells. Thermal stability is important—the melting point and glass transition temperature must be sufficiently high that solar cell fabrication can be completed, and the finalized cell is stable in use. Most of the work in this area is in its infancy, despite work in the late 1990s on the surface chemistry of organic molecules on CdTe (Cohen et al. (1998))\textsuperscript{217,218}.

An early reference found to J-V results on an organic back contact for p-type CdTe solar cells is by Jarkov (2011)\textsuperscript{219} (Tallinn University of Technology). This study used PEDOT:PSS (poly(3,4-ethylenedioxythiophene): poly(-styrenesulfonate)) with conductivity enhancing additives, which gave a (Cu-free process) PCE of 3.8% ($V_{oc}$ 610 mV,
\[ J_{sc} \] 17.8 mA cm\(^{-2}\), and FF 36\%). However, the highest PCE of the reference process was only 6.6\%. Later Wang et al (2016)\(^{220}\) obtained 5.5\% (\(V_{oc}\) of the reference process was only 6.6\%). Later Wang treated CdTe, before Mo contact deposition. Some increase 21.4 mA cm\(^{-2}\), and FF 60\%).

Previous treatment with Bromine-methanol etching before PEDOT:PSS deposition and FF 48\%) with the most highly doped of their samples. Jarkov et al (2013)\(^{221}\) later tried electrodeposition of poly-pyrrole-based back contacts: obtaining 10.4\% PCE for poly-pyrrole doped with \(\beta\)-naphthalene sulfonate (\(V_{oc}\) 739 mV, \(J_{sc}\) 20.9 mA cm\(^{-2}\), and FF 67.1\%). Earlier work by Koll et al (2011)\(^{222}\) at the University of Toledo had shown pyrrole surface treatments to leave the surface Te-rich, as well as having a possible pinhole filling role. Ferekides and Morel (2011)\(^{177}\) published a summary report of a contract which looked at many back contact technologies, including the effect of several polymer materials used as back-interface materials with Mo metal contacts. The justification for their use was given in terms of surface dipole modification of the metal work function. The summary report gives little detail on materials, methods, or results, and the polymer work was stated to be “for all practical purposes very preliminary.” Polymers derived from the monomers 4-methoxybenzoic acid (p-anisic acid), 4-chlorobenzoic acid, and 4-cyanobenzoic acid were spin-coated onto CdCl\(_2\) treated CdTe, before Mo contact deposition. Some increase in \(V_{oc}\) was observed but the device technology was not optimized to minimize series resistance. No results for these polymers are included in the organic back contacts summary given in Table 10.

Spiro-OMeTAD (N\(_2\),N\(_2\),N\(_\prime\),N\(_\prime\),N\(_7\),N\(_7\),N\(_\prime\),N\(_\prime\)-octakis(4-methoxyphenyl)-9,9’-spirobi[9H-fluorene]-2,2’/7,7’-tetramine) is another common HTM used in DSSC and perovskite solar cells. Spiro-OMeTAD hole mobility is very low (~10\(^{-5}\)-10\(^{-3}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\)), so a higher conductivity material is required on top. Spiro-OMeTAD is commonly doped and oxidized to increase conductivity. A very common dopant contains lithium,\(^{224}\) which could diffuse into the CdTe and affect the cell stability. Du et al (2015)\(^{225}\) saw an improvement in nanocrystal CdTe solar cells when using spiro-OMeTAD as a replacement HTM for MoO\(_3\). Shalvey et al (2018)\(^{226}\) saw that Li-doped spiro-OMeTAD reduced forward-bias rollover in CdTe solar cells, but increased ambient temperature series resistance, resulting in no increase in PCE. Research on improving spiro-OMeTAD and similar materials intended as perovskite HTMs could also possibly benefit CdTe solar cells.

P3HT (Poly(3-ethylthiophene-2,5-diyl)) was found by Major et al (2017)\(^{227}\) to act as a pinhole blocker and a back contact material. Shunt resistance was significantly improved, giving better yield and reduced FF spread. P3HT/CdTe interface has also been examined in CdTe quantum dots.\(^{228}\) Abdul-Manaf et al (2014)\(^{229}\) used polyaniline as a pinhole blocking layer. Separating out pinhole blocking and back contact interface effects is not trivial, and no study to date has given a comprehensive treatment of this issue.

Doped P3HT, with a similar HOMO level to spiro-OMeTAD, gave similar results\(^{226}\) to spiro-OMeTAD. However, Shalvey et al (2018),\(^{226}\) also tried PFO (Poly(9,9-di-n-octylfluorenyl-2,7-diyl)), which has a much deeper HOMO level, and found a reduced PCE (9.8\%), with enhanced forward-bias rollover.

Another way of viewing the use of an organic intermediate layer between the CdTe and the metal back contact is as a method of modifying the metal work function (de Boer et al (2005)\(^{230}\)). Exact metal work functions often depend on crystal face.

Cobalt phthalocyanine (CoPC) contacts were used by Paudel and Yan (2014)\(^{231}\) achieving 14.3\% PCE (\(V_{oc}\) 815 mV, \(J_{sc}\) 24.2 mA cm\(^{-2}\), FF 72.3\%, and \(R_s\) 2.7 \(\Omega\) cm\(^{-2}\)) in a device free of forward-bias rollover. Maximum \(V_{oc}\) was found to be for a 10 nm thick CoPC layer. Copper phthalocyanine (CuPc) has been used as a HTM in perovskites (eg, Ke et al (2015)\(^{232}\) PCE 14.7\%) but only in 2019 (Varadharajaperumal et al (2019)\(^{233}\)). It was used as a CdTe solar cell back contact. In a process with a low 1.3\% baseline efficiency, a PCE of 2.7\% was achieved.

### Table 8

<table>
<thead>
<tr>
<th>Reference</th>
<th>Material</th>
<th>(V_{oc}) (mV)</th>
<th>(J_{sc}) (mA cm(^{-2}))</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yanagi et al (2007)(^{191})</td>
<td>BaCuTeF</td>
<td>540</td>
<td>4.8</td>
<td>46</td>
<td>1.2</td>
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<td>Yamamoto et al (2015)(^{194})</td>
<td>BaCuSeF</td>
<td>805</td>
<td>22.1</td>
<td>55.7</td>
<td>9.9</td>
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<td>Miki et al (2018)(^{197})</td>
<td>BaCuSF/ITO</td>
<td>818</td>
<td>25.2</td>
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<td>13.9</td>
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<td>Kitabayashi et al (2017)(^{195})</td>
<td>SrCuSeF/ITO</td>
<td>804</td>
<td>27.5</td>
<td>65</td>
<td>14.3</td>
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<td>Wada et al (2018)(^{196})</td>
<td>SrCuSeF:NaITO</td>
<td>806</td>
<td>27.5</td>
<td>66.1</td>
<td>14.7</td>
</tr>
<tr>
<td>Bhandari et al (2017)(^{198})</td>
<td>Cu/MAPb(0.1(<em>{I</em>{0.9}}))(_{3})/Au</td>
<td>838</td>
<td>19.6</td>
<td>77.2</td>
<td>12.7</td>
</tr>
<tr>
<td>Bhandari et al (2017)(^{198})</td>
<td>Cu/MAPb(0.3(<em>{I</em>{0.7}}))(_{3})/Au</td>
<td>836</td>
<td>20.2</td>
<td>77.5</td>
<td>13.1</td>
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<tr>
<td>Bhandari et al (2017)(^{198})</td>
<td>Cu/MAPb(0.5(<em>{I</em>{0.5}}))(_{3})/Au</td>
<td>839</td>
<td>19.3</td>
<td>77.8</td>
<td>12.6</td>
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<td>Bhandari et al (2017)(^{198})</td>
<td>Cu/MAPb(0.7(<em>{I</em>{0.3}}))(_{3})/Au</td>
<td>841</td>
<td>20.0</td>
<td>77.1</td>
<td>13.0</td>
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<td>X. Li et al (2019)(^{200})</td>
<td>CuI</td>
<td>795</td>
<td>25.4</td>
<td>71.9</td>
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The performance potential of metal phthalocyanines as back contacts in CdTe has not been fully explored. Phenyl-C61-butyric acid methyl ester (PCBM), which contains a fullerene group, was used by Walkons et al (2014) as a CdTe back contact layer and gave a low maximum PCE of ~3% (Voc, Jsc, and FF were all poor); a back contact barrier height of 0.6 V was estimated from series resistance vs temperature measurements.

Pentacene was investigated by Perrenoud (2012)—a PCE of 8.8% was obtained with no etching and no copper applied (low Jsc is possibly due to poor quality glass/TCO used in this experiment). Undoped pentacene is a p-type semiconductor; derivatives can have high hole mobilities for organic materials (>1 cm² V⁻¹ s⁻¹).

Swartz et al (2019), in a set of experiments using CdTe nanoparticles as cavity fillers in CSS-grown CdTe absorber devices, tried another proven perovskite hole contact material, spin-coated EH44 (2,7-Di(N,N-dimethoxyphenylamino)-N-(2-ethylhexyl)carbazole), as an interlayer between CdTe and a gold metallization achieving PCE 15%. EH44 is believed to have a glass transition temperature of only 69°C (lower than spiro-OMeTAD) but unencapsulated perovskite stability at 50°C was improved with EH44 compared to spiro-OMeTAD.

Table 10 shows CdTe solar cell performance results with organic materials as back contacts. Voc values above 700 mV are achieved with all materials, raising Voc above 800 mV appears more challenging with organic back contacts. Jsc values are often good, vertical transport of carriers through very thin organic layers is good enough. Achieving FF above 70% appears difficult: low mobility values require very thin layers to avoid significant increases in series resistance.

It is beyond the scope of this review to examine the valence band offsets to CdTe for every material in this review.

### Summary

The search for an ideal back contact for p-type CdTe solar cells has not yet found a single solution. While back contact quality is not the only limiting factor in CdTe absorber cell performance, choosing poor contact materials can limit photovoltaic conversion efficiency or lead to degradation over time.

If the highest efficiency is required, a metallic or near metallic conductivity is necessary. At the same time, the interface must have a low defect density to avoid excessive carrier recombination. An ideal back contact will act as an electron reflector. Carriers need to arrive at the rear contact, so high carrier lifetime within the CdTe is a precondition, as well as a low density of defects at grain boundaries and the rear interface.

Similarities between the CdTe back contact issue and the hole transport layer in perovskite solar cells are noted. The range of organic materials used as HTMs in the extensive but less mature perovskite solar cell literature is already large. Concerns common to CdTe and perovskite solar cells include the thermal stability of the contact material itself, encapsulation, maximizing transport layer conductance, dopant diffusion, and cost of materials. Wide-gap perovskites are often aimed at tandem cell architectures and therefore require high NIR transparency. The following nonexclusive list of inorganic materials has been used as back contacts for both CdTe and perovskite solar cells: MoO₃, NiO, CuO, MoS₂, V₂O₅, NiS, CuSCN, CuI, CuPc, and carbon allotropes. Organic HTMs used on perovskite materials are too numerous to mention here and have been reviewed recently by Urieta et al (2018) and Pitchaiya et al (2020). A small fraction of these organic materials already has been used as CdTe back contacts—a systematic approach to their trial would be useful considering not
only band alignment but also their long-term stability and compatibility with a metal or other very high conductivity material. The only inorganic perovskite HTMs mentioned by Pitchaiya et al not known to have been used on CdTe are CuCrO2 and CuGaO2.

The ability to dope p-type CdTe using group V elements up to and above the 10^{16} \text{cm}^{-3} level allows the back contact to be decoupled from the requirement for including copper-containing compounds in the back contact structure: A wider choice of materials is available.

Ultimately, material costs matter, and any expensive materials removed from a process. In terms of impure elements, tellurium cost is expected to be the largest single component of the materials bill of thin film CdTe solar cells. Expensive metals such as gold or platinum are useful in fundamental studies but too costly in production. As tellurium is a moderately rare element itself, a crude guide is that any material used in the CdTe cell should cost significantly less than Te.

Promising materials include thin interlayers of stable materials that will not diffuse out to dope CdTe. Organic layers offer the widest range of tuneability but need to be engineered to be stable at subsequent processing temperatures. Other suggestions for further trial include Bi₂Te₃ on arsenic-doped CdTe; MoS₂/Ni, copper-free thiocyanates and phthalocyanines, and a wider selection of perovskite like halides than has been tried until now.

ACKNOWLEDGMENTS

The authors acknowledge funding from Innovate UK and EPSRC (project reference number EP/R035997/1), and support from the European Regional Development Fund, through the Welsh Government, for the 2nd Solar Photovoltaic Academic Research Consortium (SPARC II).

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REFERENCES


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<th>Reference/comments</th>
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<th>( V_{oc} ) (mV)</th>
<th>( J_{sc} ) (mA cm(^{-2}))</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>( R_s ) (Ω cm(^2))</th>
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<td>66.5</td>
<td>14.25</td>
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<td>767</td>
<td>22.8</td>
<td>65.7</td>
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<td>22.3</td>
<td>70.8</td>
<td>12.26</td>
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<td>Wang et al (2016)(^{220})</td>
<td>PCBM/Pt</td>
<td>700-800</td>
<td>21 (at best, estimated)</td>
<td>low</td>
<td>~3</td>
<td>~100</td>
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<td>610</td>
<td>17.8</td>
<td>36.0</td>
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<td>72.3 (est.)</td>
<td>12.65</td>
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<td>750</td>
<td>25.3</td>
<td>50</td>
<td>9.81</td>
<td>-</td>
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</table>


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**How to cite this article:** Hall RS, Lamb D, Irvine SJC. back contacts materials used in thin film CdTe solar cells—A review. Energy Sci Eng. 2021;9:606–632. https://doi.org/10.1002/ese.3.843