Large-Scale Transparent Photovoltaics for a Sustainable Energy Future: Review of Inorganic Transparent Photovoltaics

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ABSTRACT

Transparent photovoltaics (TPVs) are a crucial energy platform for harvesting solar energy in windows, enabling onsite power generation for widespread applications in buildings, vehicles, displays, sensors, and the Internet of things. TPV devices are fabricated using eco-friendly processing methods and materials, and must perform stably for an adequate societal impact. This review article is focused on the emerging TPV devices made of inorganic materials, including oxides and two-dimensional sulfides. Herein, we briefly review the wide-bandgap inorganic TPVs and their performances. Specifically, the sputtering method is considered for the large-scale and eco-friendly preparation of inorganic heterostructures.

Keywords: Transparent photovoltaic, Inorganic thin film, Onsite power generation, Large-scale fabrication

1. Introduction

The two outcomes of the industrial development in the modern era, viz. a high energy demand and global warming, have compelled the technologists to turn to naturally available and environment-friendly sources of renewable energy. Figure 1(a) indicates a growth in global electricity production, using renewable energy sources, from 24.5 (2016) to 26.3% (2018) [1]. Among the sources of renewable energy, electricity production from wind and solar energy showed a remarkable increase from 4.0 to 5.5% and 1.5 to 2.4%, respectively, between 2016 and 2018, indicating the focus that these technologies have received in the recent years. Photovoltaic technology has the capacity to meet the requirements of the future energy demand of humankind with a reduced environmental impact. The amount of energy that the Sun delivers to Earth per hour is approximately equal to the total energy consumption of humanity per year ($\sim 5 \times 10^{20}$ J in 2018) [2–5]. In the recent years, photovoltaic technology has undergone commendable improvements, resulting in the development of highly efficient, low-cost, and environment-friendly solar cells. These achievements have been realized by modifying both the fabrication processes and materials used. The current renewable energy trends indicate that the renewable electricity production will exceed the energy production from fossil fuels by 2026. Likewise, in 2040, two-thirds of the global electricity supply is expected to be derived from renewable sources. Expectedly, solar and wind power would produce 40% of the energy used, and the other renewable energy sources, including hydropower and bioenergy, would account for 25% of the total energy production [1].

At present, 95% of the photovoltaic device market is controlled

by Si-wafer-based solar cells, which are first-generation products. To improve the efficiency–cost ratio, second-generation cells, based on the thin-film technology, have been introduced. Thin-film solar cells made of cadmium telluride, copper indium gallium sulfide, and copper zinc tin sulphur selenide show efficiencies of 22.1, 22.6, and 12.6%, respectively [18–22]. The emerging photovoltaic techniques are included in the third generation of solar cells, mainly perovskite, tandem, dye-sensitized, organic, and quantum-dot solar cells with power conversion efficiencies (PCEs) of 25.2, 29.1, 12.3, 17.4, and 16.6%, respectively [18, 23, 24].

However, the large surface area, required for the installation of these opaque photovoltaics, is a hindering factor for the energy requirements of humankind. Thus, transparent photovoltaic (TPV) cells

Figure 1. Global energy scenario and TPVs. (a) Comparison of global electricity production, using different sources, for 2016 and 2018 [1]. (b) Highest PCE reported for various TPVs along with their AVT values [6–17].

Table I. AVT values and photovoltaic performance of different types of TPV devices, indicating the short-circuit current densities (J_{sc}), open-circuit voltages (V_{oc}), fill factors (FF), efficiencies (η), and active areas (A) of the devices.

TPV	AVT (%)	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	η (%)	A (mm ²)	Ref.
SP-DSSC	60	16.25	779	73	9.2	–	[7]
NIR-OSC	43	15.8	680	66	7.1	–	[10]
PSC	66	12.60	770	54	5.28	10	[11]
PVSC	77	17.5	1025	71	12.7	39	[28]
EPD-DSSC	55	14.23	680	71	7.1	25	[13]
DC-DSSC	70	16.17	738	69	8.22	–	[14]

are attracting significant interest in photovoltaic research because of their wide application as building-integrated, building-applied, and vehicle-integrated photovoltaic devices [25,26]. Hence, TPV technology could aid in the conversion of the largest energy consumers into the largest power plants. In conventional solar cells, the absorption of visible light leads to the generation of electron–hole pairs that produce current. In contrast, TPVs allow the visible light to pass through and generate current by absorbing ultraviolet (UV) light photons. Therefore, TPV devices meet our high energy demands as well as block the hazardous part of the electromagnetic spectrum. The Shockley–Queisser maximum theoretical efficiency limit for a TPV is ~20%, whereas for the conventional photovoltaics (CPVs), this limit is ~32% [26,27]. Although the TPVs exhibit low PCEs than do the CPVs, their features like transparency, onsite power production, protection from high-energy photons like UV, and high flexibility paved a new pathway for the widespread application of TPVs.

Table I shows a comparison of the photovoltaic performance of different types of TPVs along with their average visible-light transmittance (AVT) values. Figure 1(b) compares the reported highest PCE and AVT values for different types of TPVs (AVT > 40%) such as screen-printed dye-sensitized solar cells (SP-DSSC), near-infrared-organic solar cells (NIR-OSC), polymer solar cells (PSCs), perovskite solar cells (PVSC), electrophoretic deposition dye-sensitized solar cells (EPD-DSSC), and dip coated-dye sensitized solar cells (DC-DSSC) [6, 7, 10, 11, 13, 14, 28, 29]. Among these, the highest PCE, i.e., 12.7% (AVT of 77%), is exhibited by the perovskite solar cells with a device configuration of TiO₂/MAPbI₃/spiro-OMeTAD/AgNW (where NW represents nanowire). However, the use of conventional organic spiro-OMeTAD in the device configuration as a hole transport layer hinders its further development owing to the complex synthesis procedure, high cost, and instability. The commercially available spiro-OMeTAD is nearly 23 times more expensive than Au and Pt, by its weight percentage [30]. Hence, although these devices exhibit high PCEs (> 4%), their toxicity and high costs, along with the low stability of their organic molecules, are the major limitations of these devices. Consequently, the recent investigations in the field of TPV technology have been focused either on overcoming these hurdles by introducing suitable alternatives or moving toward inorganic TPV technology. Thus, inorganic TPV technology has become more attractive because of the incorporation of wide-band-gap metal oxides as the active UV layer.

Wide-band metal oxides are promising candidates in the search for naturally available and acceptable semiconductor materials, in the field of inorganic TPVs [31–33]. Figure 2 presents a schematic diagram of an inorganic TPV. It consists of top and bottom transparent electrodes, separated by a surface field layer, and wide-band-gap metal oxides with n-type conductivity, such as ZnO, TiO₂, and so forth, and those with p-type conductivity, such as NiO, CuAlO₂, and Cu₂O. The wide band gaps of these materials allow visible-light transmittance and UV-light absorbance, which are the underlying principles of TPV applications. Incident UV photons with energies higher than the band gap of the materials result in the formation of electron–hole pairs. Further, charge separation is achieved using built-in electric fields generated by the p–n heterojunction. The separate extraction of these charge

carriers to the external circuit results in the generation of electricity. The surface field layer prevents the recombination of the minority carriers.

A literature review indicated that inorganic TPVs have attracted considerable research interest since 2013 because of the improvements in photovoltaic performance, facilitated by the incorporation of various mechanisms, to overcome the factors that limit device efficiency [15,33–43]. Over the past few years, several research groups have reviewed the technologies underlying TPVs, semi-transparent thin-film TPVs, and organic TPVs [6,26,44–46]. However, no reports are available on inorganic TPVs. Thus, considering the promising aspects of inorganic TPVs, in this review article, we focus on the fabrication and mechanisms of inorganic TPVs, along with the improvements in their performance (AVT < 40%), which may provide support to the future investigations for attaining commercially acceptable cost–efficiency ratios. In the TPVs, the p–n heterojunction is typically prepared using the reactive sputtering technique, and consequently, this review article highlights the optoelectrical properties of the reactive-sputtered wide-band-gap metal-oxide films.

2. Wide-band-gap metal oxides for inorganic TPVs

Some widely used wide-band-gap metal oxide materials are NiO, Cu₂O, and Cu delafossite (CuGaO₂, CuCrO₂, CuFeO₂, and CuFeO₂), which are p-type materials, and ZnO, AZO, TiO₂, SnO₂, and Zn₂SnO₄, which are n-type materials. Table II compares the optical and electrical properties of these metal oxides along with their deposition parameters [37,39,47–59]. Figure 3 presents an energy-level diagram of both the p-type and n-type metal oxides [33,60–66].

NiO has a rock salt crystal structure with octahedral Ni²⁺ and O^{2–} sites. It exhibits a wide band gap in the range of 3.5–4 eV, allowing a higher transmission of visible light, p-type conductivity, large absorption coefficients (10⁵ cm^{–1}), high stability, and high work function (~5.0 eV) [30,68]. Due to its low electron affinity (1.33–1.85 eV), a

Figure 2. Schematic illustration of inorganic TPVs enabling onsite power production and transparent device fabrication.

Table II. Processing parameters and optical and electronic properties of metal-oxide films grown using different sputtering methods, where E_g is band gap, T is transmittance, t is thickness of the film, T_p is processing temperature, σ is conductivity type (n -type or p -type), ρ is resistivity, μ is mobility, and N is carrier concentration.

Material	Processings parameters	T_p (°C)	t (nm)	σ	E_g (eV)	T (%)	ρ ($\Omega\cdot\text{cm}$)	N (cm^{-3})	μ (cm^2/Vs)	Ref.
NiO	~150 W(RF) pO ₂ ~0.5%	25	300	p	3.5–4	80	10 ⁴	10 ¹⁴	50	[37]
	~200 W(DC) Ar:O ₂ ~70:3	25	120	p		—	9665	6.42×10 ¹⁴	1.01	[52]
	Power ~50 W	25	100	p	3.8	80	1503	6.08×10 ¹⁴	6.73	[53]
		400	60	p	3.2	60	72	3.87×10 ¹⁶	2.23	
Cu ₂ O	~720 W/cm ² (DC) Ar:O ₂ ~90:10	350	400	p	2.48	—	22	4.41×10 ¹⁸	57.5	[54]
CuGaO ₂	250 W pO ₂ ~45%	750	686	p	3.45	poor	57.4	—	—	[55]
		700	500	p	3.6	80	15	1.7×10 ¹⁸	0.23	[56]
CuCrO ₂	~200 W pN ₂ ~40%	625	150	p	3	73	53	1.46×10 ¹⁹	0.8	[57]
	Power ~ 250 W pO ₂ ~70%	625	—	p	3.14	65	4.31	4.17×10 ¹⁸	1.22	[58]
CuFeO ₂	~4 W/cm ² pO ₂ ~1%	25	130		3.25	60	11.76	2.80×10 ¹⁷	1.89	[59]
CuAlO ₂	~750 V(DC) pN ₂ 6×10 ⁻² pa	300	—	p	3.46	69	1.95	4×10 ¹⁷	9.4	[47]
ZnO	~200 W	25	240	n	3.2	—	3.5×10 ³	—	1	[48]
	~300 W	25	470	n	3.3	70	—	5×10 ¹⁷	—	[39]
AZO	Al ₂ O ₃ :ZnO ~0.5 ~225 W	330	640	n	3.66	70	4.3	3.6×10 ²⁰	41.3	[49]
	2% of Al in ZnO ~300 W	550	15	n	3.42	70	—	1.5×10 ²⁰	3	[39]
TiO ₂	~300 W Ar ~50 sccm O ₂ ~2 sccm	500	5	n	3.2	70	0.1	3×10 ¹⁹	0.1–4	[43]
SnO ₂	~30 W, Ar ~60 sccm O ₂ ~9 sccm	150	300	n	3.6–4	80	0.0419	3.57×10 ¹⁹	3.37	[50]
Zn ₂ SnO ₄	~50 W Ar:O ₂ ~99:1	300	100	n	3.65	~60	2.1	10 ¹⁷	14.5	[51]

thin NiO film induces the effect of electron blocking with a high carrier mobility ($\sim 1\text{--}10\text{ cm}^2/\text{Vs}$), i.e., an efficient hole-transporting property [52, 53]. The high exciton-binding energy (110 meV) of the NiO films enables a lower thermalization loss of the exciton [69]. These excellent optical and electrical properties make it a suitable material for a wide range of applications, such as an anode buffer layer in organic solar cells, a hole transport layer in PSC, radiation detectors, laser materials, thermoelectric devices, and so forth. Further tuning of the electrical properties (carrier concentration, hole mobility, and work function) is attained through doping with Cu⁺, Ag⁺, Cs⁺, Li⁺, and Mg²⁺, which can improve the reported PCE of the PSCs [30, 70, 71]. Although NiO thin films have been prepared using various wet chemical routes, chemical vapor deposition, and physical vapor deposition, TPV technology is mainly focused on large-scale preparation methods like reactive sputtering [33, 39, 68]. Sputtering techniques have the advantage of realizing higher uniformity over a large surface area, a higher film density, and stronger adhesion. Warasawa *et al.* [37] prepared NiO films using the radio frequency (RF) reactive sputtering technique for TPVs in which an RF power of 150 W was applied to the Ni target in the presence of Ar and O₂ gases with an O₂ fraction (O₂/(Ar+O₂)) of ~0.5%; the prepared film exhibited a comparatively high mobility of ~50 cm²/Vs. They reported a decrease in AVT from 80 to 50 % with a decrease in the electrical resistivity from 10⁴ to 10³ $\Omega\cdot\text{cm}$. NiO consists of both Ni²⁺ and Ni³⁺ oxidation states, and its p -type conductivity is improved by increasing the concentration of Ni³⁺, via an O-rich growth condition. This condition results in the formation of Ni vacancies (V_{Ni}) and/or interstitial O in the NiO crystal lattice. How-

ever, the increased V_{Ni} concentrations result in a decrease in the AVT because of the visible light absorbance of Ni³⁺. Hence, the preparation of NiO films, using the reactive sputtering technique under a high O₂ fraction, results in a decrease in the AVT (~40%) with an increase in the p -type conductivity [37].

Cuprous oxide (Cu₂O) is a well-known p -type semiconductor with a comparatively high band gap of 2.38–2.51 eV, high carrier mobility, high diffusion length, and high work function (~5.0 eV). It has a cubic crystal structure, and each unit cell consists of four Cu (at the fcc position) and two O atoms (at tetrahedral sites). The p -type conductivity of Cu₂O is due to the presence of Cu vacancies (V_{Cu}) [60, 72].

Cu delafossite metal oxides, such as CuGaO₂, CuCrO₂, CuAlO₂, and CuFeO₂, have recently attracted significant attention as suitable materials for hole transport layers in PSC. The delafossite metal oxides have an A⁺B³⁺O₂ structure, in which a sheet of monovalent A ions are stacked between the edge-shared octahedral BO₆ ions. The Cu delafossite metal oxides are p -type semiconductors with low electron affinities (~2.1 eV), high carrier mobilities (~100 cm²/Vs), and large diffusion lengths [30]. These materials exhibit a direct energy band gap in the range of 3.2 to 3.6 eV, with a high visible-light transmittance (~80%), which makes them a suitable choice for TPVs. The p -type conductivity of these materials is correlated with the formation of Cu defects and O interstitials [73]. Yu *et al.* [55] prepared CuGaO₂ thin films using a reactive magnetron sputtering technique, in which a sputtering power of 250 W was applied to Cu and Ga targets in the presence of Ar and O₂ as the sputtering gases (O₂/(O₂+Ar) at ~45%) at room temperature, followed by annealing (700–900°C) in an N₂ at-

Figure 3. Energy-level diagram of widely used p-type (NiO [33], Cu₂O [60], CuGaO₂ [61], CuCrO₂ [62], and CuAlO₂ [63]) and n-type (ZnO [33], AZO [64], TiO₂ [65], SnO₂ [67], and ZTO [66]) metal oxides.

mosphere. At an annealing temperature of 700°C, both the CuO and CuGaO₄ phases are formed along with CuGaO₂, whereas in the temperature range of 750–850°C, a single phase of CuGaO₂ is formed. A further increase in the annealing temperature results in the formation of Ga₂O₃ at a secondary phase. The prepared single phase of the CuGaO₂ film (annealed at 750°C) exhibits a direct energy band gap of 3.45 eV, whereas the film annealed at 700°C exhibits a direct energy band gap of 2.44 eV [55]. For the application of TPVs, Tonooka *et al.* [36] prepared CuAlO₂ films using the pulsed layer deposition (PLD) technique with a substrate temperature of 400°C in the presence of 2 mTorr of O₂. The deposited film exhibited both direct and indirect band gaps of 1.8 and 3.5 eV, respectively, with an electrical resistivity of ~10 Ω·cm. They reported that the amorphous nature of the prepared film results in an increase in the indirect optical absorption with a shift in the absorption edge toward the lower energy side.

Table II shows a comparatively high reaction temperature for CuCrO₂ and CuGaO₂, and such a high temperature is disadvantageous for the real-life applications of TPVs. In contrast, Zhang *et al.* [61] prepared CuGaO₂ nanoplates using a microwave-assisted hydrothermal method (reaction temperature ~230°C, reaction time of ~2 h). Later, the spin coating (3,000 rpm for 60 s, followed by drying at 100°C for 1 h) technique was used for the preparation of CuGaO₂ films. Furthermore, PSCs, fabricated with a device configuration of FTO/TiO₂/CH₃NH₃PbI₃₋₁Cl₃/CuGaO₂/Au (where FTO is fluorine-doped tin oxide), exhibited a PCE of 18.51%. Similarly, Jeong *et al.* [62] used a low-temperature hydrothermal method (at a reaction temperature of 240 °C, with a reaction time of 60 h) for the preparation of CuCrO₂ as a hole transport layer for PSCs with a PCE of 13.1%. Thus, a wet chemical route is another suitable low-temperature pathway for the preparation of high-formation-temperature metal oxides.

ZnO has garnered significant attention as an n-type material for a wide range of applications. ZnO has a wurtzite hexagonal crystal structure with a direct energy band gap of ~3.2 eV, high electron mobility, and large exciton binding energy (60 meV), rendering it feasible for the fabrication of p–n heterojunctions [64]. The tetrahedral coordination in ZnO results in a non-symmetric structure with piezoelectric and pyroelectric properties. Patel *et al.* [69] prepared ZnO films for TPV applications, using a sputtering technique with an RF power of 300 W applied to the ZnO target.

TiO₂ is another widely used n-type polymorphic semiconductor with anatase, brookite, and rutile crystal structures. Among these, the rutile structure is highly stable at macroscopic sizes, whereas the anatase occurs only in nanoscopic sizes. Brookite is the rarest naturally occurring form of TiO₂. Anatase-TiO₂ exhibits a direct energy band gap of 3.2 eV with an electrical resistivity of ~0.1 Ω·cm, a donor concentration of ~10¹⁷ cm⁻³, and a bulk mobility in the range of 0.1–4.0

cm²/Vs [74]. Patel *et al.* [34] prepared TiO₂ films using direct current (DC) reactive sputtering with a DC power of 300 W applied to a Ti target in the presence of an Ar and O₂ flow rate of 50 and 2 sccm, respectively, at a substrate temperature of 500°C.

Sn-based metal oxides are attractive owing to their excellent optoelectronic properties, which are either similar to or better than those of TiO₂. The low electron mobility of TiO₂ causes inadequate charge separation at the heterojunction. SnO₂ is a wide-band-gap (3.6–4.0 eV) n-type semiconductor with a rutile crystal structure. The highly efficient charge extraction property of SnO₂ is mainly due to its deep conduction band and high carrier mobility (100–200 cm²/Vs) [50]. Zn₂SnO₄ (ZTO) is another well-known n-type semiconductor with a wide direct-energy band gap of 3.8 eV and refractive index of ~2, which allows a high visible-light transmittance [51]. The conduction-band edge position of ZTO is similar to that of TiO₂, and it exhibits a high electron mobility of ~10–15 cm²/Vs, which allows ~10 times faster electron transport with a higher charge collection efficiency than that of TiO₂. The O vacancy (V_O) in ZTO acts as a double-ionized donor that contributes two electrons to the electrical conduction, such that the carrier concentration can be improved by annealing under a reducing atmosphere [32]. Although these Sn-based transparent conducting oxides have gained notable attention as electron-transport-layer materials for PSCs, they have not been used in TPVs until recently.

3. Photovoltaic performance of inorganic TPVs

Tonooka *et al.* [36] fabricated an ITO (200 nm)/CuAlO₂ (400 nm)/n-ZnO (400 nm)/n⁺-ZnO (200 nm) TPV (here, ITO is indium tin oxide) using the PLD technique. The fabricated device exhibited a weak photovoltage of 80 mV under a light-emitting diode (wavelength, λ ~470 nm, intensity, I ~37 W/cm²). The low performance of the device is mainly due to the amorphous nature of the CuAlO₂ film deposited at a very-low substrate temperature of 400°C. Warasawa *et al.* [37] produced an NiO-based TPV with a device configuration of ZnO:Ga (500 nm)/ZnO (100 nm)/NiO (300 nm), using the reactive sputtering technique. The fabricated device exhibited a visible-light transmittance of 70% and PCE < 0.01%. The reported low values of short-circuit current density (J_{sc}) and open-circuit voltage (V_{oc}) can be correlated with the low crystal quality of NiO films and formation of defects at the ZnO/NiO interface due to the sputtering process. Karsthof *et al.* [38] fabricated an NiO/ZnO TPV, in which the ZnO and NiO films were deposited using PLD and reactive DC sputtering techniques, respectively. The applied DC power for the Ni target was 30 W with an Ar/O₂ flow ratio of 1:1. The device, with a configuration of Al₂O₃/AZO/ZnO/NiO/Au, exhibited 46% transmittance in the visible range, with a PCE of 0.1% for solar spectrum and 3.1% for UV light illumination. The authors commented that the PCE could be further improved by reducing the density of the ZnO/NiO interface defects by introducing a buffer layer or through a surface passivation treatment.

Patel *et al.* [33] fabricated an FTO/ZnO (100 nm)/NiO(35 nm)/Ag TPV. The NiO layer was deposited using the DC reactive sputtering technique, wherein the Ni target was sputtered with a DC power of 50 W in the presence of Ar (30 sccm) and O₂ (4 sccm) gases. The prepared NiO/ZnO heterojunction exhibited a potential barrier of 0.8 eV, offering a high built-in electric field and low dark current (J_{dark}). Because J_{dark} is the movement of charges under equilibrium conditions, the low J_{dark} value indicates a better-quality interface. The high built-in electric field separated the electron–hole pairs generated through UV photon absorption at the interface. Finally, the fabricated device exhibited a visible-range transmittance of 69.6% with a PCE of 6% under UV illumination (λ ~365 nm, I ~10 mW/cm²). Further, Ban *et al.* [39] introduced an aluminum-doped zinc oxide (AZO) layer as the back surface field layer of a large-scale TPV (1 inch²), with a device configuration of FTO (500 nm)/AZO (10 nm)/ZnO (400 nm)/NiO (75

Figure 4. Oxide thin-film-based TPVs. (a) Device architecture. (b) Cross-sectional field emission scanning electron microscopy image of a TPV device with a configuration of FTO/TiO₂/ZnO/NiO/AgNW. (c) Oxide-based TPV devices. (d) Energy-band diagram showing the enhanced carrier lifetime with the incorporation of an ultrathin TiO₂ (5 nm) layer. Reproduced with permission from [78], Copyright 2020, Elsevier.

nm)/AgNW. The NiO layer was deposited under optimized sputtering conditions. The device exhibited a high visible-light transmittance of >70%. In the absence of the AZO layer, the device possessed a positive banding of 25 meV, which caused recombination of the photo-generated charge carriers. In contrast, when the AZO layer was introduced as the surface field layer, the recombination of the electrons at the top surface, owing to the introduced barrier height of -0.35 eV for holes, was prevented. Accordingly, by introducing an AZO layer, the efficiency was significantly improved from 0.42 to 3.13% under UV illumination (λ of ~ 365 nm) with an intensity of 13 mW/cm^2 . Similarly, by introducing the AZO layer, the PCE was improved from 0.38 to 0.56% under the AM 1.5 spectrum.

Rana *et al.* [40] also prepared a Cu–Cu₂O/ZnO heterojunction for a TPV with a device configuration of FTO/ZnO (250 nm)/Cu₂O–Cu (100 nm)/AgNW. The Cu–Cu₂O layer was deposited using a reactive sputtering technique with a Cu target and an applied DC power of 80 W in the presence of Ar and O₂ gases (Ar/O₂ $\sim 10:1$). The heterojunction was annealed at 300°C for 10 min, in vacuum (8 mTorr). The deposited Cu–Cu₂O/ZnO film exhibited a transmittance of 80%, which was reduced to 55% (600–1,100 nm) after annealing. The fabricated device exhibited an improvement in the PCE from 0.093 to 0.405% due to annealing ($I \sim 70 \text{ mW/cm}^2$), indicating the formation of mixed oxide phases, which in turn improved the electronic properties and charge carrier transport. In the same study, AZO was introduced as a surface field layer, with a device configuration of ITO (250 nm)/AZO (200 nm)/ZnO (200 nm)/Cu₂O (100 nm)/AgNW. The fabricated device exhibited 80% transmittance in the 600–900 nm range, with an efficiency of 0.46% ($I \sim 100 \text{ mW/cm}^2$) [41]. Patel *et al.* [42, 75, 76] also fabricated an FTO/ZnO/Co₃O₄/NiO/AgNW TPV using the sputtering technique. Energy-band diagram-based studies have shown that Co₃O₄ increases the built-in electric field and reduces the band offset of the valence band. Accordingly, the PCE was improved from 0.36 to 1.30%, under the AM 1.5 spectrum ($I \sim 100 \text{ mW/cm}^2$), by incorporating an ultrathin layer (50 nm) of Co₃O₄. However, the average visible-light (400–800 nm) transmittance was reduced from > 60% to > 30% because of the incorporation of Co₃O₄.

To improve the PCE further, Nguyen *et al.* [8, 43, 77] introduced TiO₂ as a surface field layer with a device configuration of FTO/TiO₂ (5 nm)/ZnO (470 nm)/NiO (200 nm)/AgNW, in which the metal oxide layers were deposited using the sputtering technique (Fig. 4). The incorporation of TiO₂ as the surface field layer caused a 20-fold decrease in the J_{dark} value, which in turn increased the PCE from 3.09 to 6.10% under UV illumination ($\lambda \sim 365$ nm and $I \sim 8 \text{ mW/cm}^2$).

Further, Patel *et al.* [34] enhanced the photovoltaic performance of

Figure 5. (a) Schematic diagram showing the proximity vapor-transfer deposition of SnS thin films. (b) Wafer-scale transfer of SnS films on various substrates. (c) 2D-layer embedded TPV device demonstrating onsite power production. Reproduced with permission from [34], Copyright 2019, Elsevier.

a TPV by introducing a wafer-scale two-dimensional (2D) absorber layer material in the TPV device. The device configuration was glass/FTO/TiO₂/SnS/NiO/Au film, in which the SnS nanoplatelets were prepared through a novel proximity vapor-transfer method (Fig. 5). The prepared S-rich SnS nanoplatelets had a thickness of 10–15 nm, and exhibited *p*-type conductivity with a carrier concentration of $\sim 10^{17} \text{ cm}^{-3}$. Furthermore, the SnS nanoplatelets exhibited a good performance relative to that of the TPV without SnS or with conventional SnS layers. In this device configuration, the TiO₂ layer (80 nm), deposited using the reactive sputtering method, acts as the *n*-type layer. The NiO (30 nm) and Au (20 nm) films were deposited using reactive sputtering and thermal evaporation, respectively. The prepared TPV exhibited 60% visible-light transmission with a PCE of $\sim 13\%$ under UV light ($\lambda \sim 365$ nm and $I \sim 60 \text{ mW/cm}^2$). Furthermore, the device generated an output power of 6 mW under UV light ($\lambda \sim 365$ nm and I of $\sim 70 \text{ mW/cm}^2$). Kim *et al.* [15, 79, 80] demonstrated an Si-embedded TPV with a device configuration of glass/FTO/AZO (10 nm)/ZnO (400 nm)/Si (15 nm)/NiO (80 nm), wherein the Si thin films were deposited using plasma-enhanced chemical vapor deposition (Fig. 6). This device configuration enabled photon absorption from UV to longer wavelengths owing to the introduction of a Si layer, as a functional layer with a band gap of 1.8 eV, between the ZnO and NiO films. The large barrier height at the ZnO/NiO heterojunction could be reduced with the introduction of Si, which has an intermedi-

Figure 6. Si thin-film-based TPVs. (a) Device architecture. (b) Original photograph of the large-scale device with an AVT of 40% and (c) energy-band diagram of the device with a configuration of FTO/AZO/ZnO (400 nm)/Si (15 nm)/NiO (80 nm)/AgNW. Reproduced with permission from [15], Copyright 2020, Elsevier.

Table III. Photovoltaic performance in terms of short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), efficiency (η), and device active area (A), along with the AVT values of different TPV devices. In the measurement condition light wavelength λ is in nm and light intensity (P) in mW/cm².

Configuration	AVT (%)	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	η (%)	A (mm ²)	Measurement condition	Ref.
ITO/CuAlO ₂ /n-ZnO/n ⁺ -ZnO	43	–	80	–	–	7	$\lambda=470$, $P=37$ W/cm ²	[36]
ZnO:Ga/ZnO/NiO	70	0.002	170	27	0.01	–	AM 1.5	[37]
Al ₂ O ₃ /AZO/ZnO/NiO/Au	46	0.5	520	42	0.1 η_{uv} 3.1	0.23	AM 1.5	[38]
FTO/ZnO/NiO/Ag	70	2.7	532	41.8	6	9	$\lambda=365$ nm, $P=10$	[33]
FTO/ZnO/NiO/AgNW		0.79	770	62.4	0.38		AM 1.5	
FTO/AZO/ZnO/NiO/AgNW		0.80	815	86.1	0.56			
FTO/ZnO/NiO/AgNW	70		350	26	0.42	645	$\lambda = 365$ nm	[39]
FTO/AZO/ZnO/NiO/AgNW			450	40	3.13		$P = 13$	
FTO/ZnO/Cu ₂ O-Cu/AgNW (as deposited)	80	0.412	600	26.49	0.093	100	AM 1.5	[40]
FTO/ZnO/Cu ₂ O-Cu/AgNW (annealed, 300°C, 10 min)	55	1.83	360	43.13	0.405		$P=70$	
ITO/AZO/ZnO/Cu ₂ O/AgNW	80	2.92	520	30.62	0.46	–	AM 1.5	[41]
FTO/ZnO/NiO/AgNW	60	0.728	749.2	65.71	0.36	130×65	AM 1.5	[42]
FTO/ZnO/Co ₃ O ₄ /NiO/ AgNW	30	2.041	841.8	77.14	1.33			
ITO/ZnO/NiO/AgNW	50	1.87	360	36.6	3.09	–	$\lambda=365$ nm $P=8$	[43]
FTO/TiO ₂ /ZnO/NiO/ AgNW		2	580	42.2	6.12			
FTO/TiO ₂ /SnS/NiO/Au film	60	1.145 27.36	617 764	30 42	0.212 13	2500	AM 1.5 $\lambda=365$ nm $P=60$	[34]
FTO/AZO/ZnO/Si/NiO/AgNW	40	2.75	600	29.2	4.8	144	$\lambda=365$ nm $P=10$	[15]
		2.70	598	34	0.55		AM 1.5	

ate binding energy and thus improves the charge carrier transport. The fabricated device exhibited an improvement in the PCE from 0.065 to 0.560% owing to the introduced Si layer. These results indicate that the introduction of a wafer-scale 2D or Si layer as an absorber layer is a promising alternative technique to enhance the PCE of TPVs. The photovoltaic performance and AVT of various inorganic TPVs measured under the illumination of the AM 1.5 spectrum and light of $\lambda \sim 365$ nm are compared in Table III and Fig. 7.

Klochko *et al.* [35] fabricated a Cu/FTO/ZnO/NiO/Cu TPV. The 1D ZnO nanorod arrays were prepared through cathodic electrochemical deposition, and the NiO thin films were deposited using the successive ionic layer adsorption and reaction technique. However, the device exhibited a low photovoltaic performance, possibly because of

the high series resistance and diode ideality factor.

4. Conclusions

This study was performed to investigate the potential of inorganic TPVs to meet the global energy requirements with a reduced environmental impact. Inorganic TPV technology has the ability to produce cost-effective and highly stable solar cells with higher efficiency to convert the largest energy consumers, such as buildings and vehicles, into the largest energy producers. In the recent years, the semiconductor technology has been advanced with the introduction of various wide-band-gap metal oxides that have excellent optoelectrical properties and can be used in various photovoltaic applications. Among these materials, NiO/ZnO heterojunctions with AVT and PCE values of 70.00 and 0.56%, respectively, or Cu₂O/ZnO heterojunctions with AVT and PCE values of 80.00 and 0.46%, respectively, have become the focus of inorganic TPV research. The addition of an AZO layer as the surface field layer plays a significant role in improving the photovoltaic performance of both the NiO- and Cu₂O-based TPVs. Further, the introduction of a surface field layer of TiO₂ in NiO/ZnO-based TPVs yields $J_{dark} \sim 0.22$ nA, whereas an AZO layer yields a J_{dark} of ~ 1 –5 nA, which reveals the superiority of the TiO₂ surface field layer over the AZO one. The enhanced photovoltaic performance due to the incorporation of SnS nanoplatelets, with a device configuration of FTO/TiO₂/SnS/NiO/Au film, as well as due to Si, with a device configuration of FTO/AZO/ZnO/Si/NiO/AgNW, has paved a new path toward the development of cost-effective TPVs with improved efficiencies. The highest efficiency achieved to date is 0.56%, with a device configuration of FTO/AZO/ZnO/NiO/AgNW.

Figure 7. Graph comparing the PCE (under an AM 1.5 spectrum) and AVT values of various inorganic TPVs, measured under: (a) AM 1.5 spectrum and (b) light with $\lambda \sim 365$ nm.

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Conflicts of Interest

The authors declare no conflicts of interest.

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