



Review Review of the Chosen Methods of Producing Front Contacts to Transparent Conductive Oxides Layers in Photovoltaic Structures

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Abstract: It is well known that PV thin films can be deposited by an extensive range of more or less expensive and complicated techniques (such as sputtering, chemical vapor deposition (CVD), physical vapor deposition (PVD), pulsed laser deposition, atomic layer deposition (ALD)). The present paper focuses on TCO layers applied by chosen techniques, including mainly the ALD and CVD methods. Thin layers of transparent conductive oxides constitute a well-known group of materials with unique properties. Oxides such as ZnO, SnO₂, and In₂O₃ are the most significant materials of this type; some of them are discussed in the paper. From the application point of view in the photovoltaic industry, the goal is to apply a method that will provide the highest value of electric charge conductivity while maintaining the minimum value of absorption in the layer and a reduced value of the reflection coefficient. The implementation of significant achievements in the coming decade is for developing guidelines for metallization processes and TCO layers deposited by the ALD method. The work contains chosen engineering processes, including the fabrication of transparent conductive oxides (TCO) thin films applied to silicon substrates by ALD and CVD for application as emitter conductive coatings in photovoltaic structures and the fabrication front metallization of solar cell using different techniques, including among others laser techniques. Moreover, the work also contains predictions about solar cells, which will be among the most prevalent solar cells in mass production using thin- and thick-film technology.

Keywords: transparent conductive oxides (TCO); atomic layer deposition (ALD); solar cells

1. Introduction

Progress in producing photovoltaic cells with ever-higher efficiency has been made in recent years, mainly thanks to modern techniques and materials, enabling the intensive development of individual stages of their production [1]. Innovative, which cannot be seen at first glance, able to effectively convert sunlight into electricity, turn out to be transparent conductive layers—transparent to light and at the same time perfectly conductive to electricity [2]; the photovoltaic sector (PV) has enormous development potential, and can be considered a new and extremely promising branch of the global industry. The most significant factor in the growth of the photovoltaic market is the constant reduction of the cost of obtaining 1 W_p of power from the energy converter. This means that producers of PV panels/modules must achieve higher energy conversion efficiency parameters, namely increasing the conversion efficiency of the solar cell and the photovoltaic (PV) module, as well as reducing costs in the process of production [3].

The sun is an inexhaustible energy source, so the current challenge that scientists worldwide are facing is to increase the efficiency of cells—maximize the value of the quotient: cell efficiency/production cost. The development of photovoltaics is the answer to the growing demand of the energy sector for new renewable electricity solutions, primarily due to the energy transition in Poland resulting from the global pandemic and the war



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). with Ukraine. However, this development will not be possible without systemic solutions, i.e., financial support from the state and local authorities and research work in this area (Table 1). Renewable sources are slowly beginning to play an increasingly important role in this development, but also gas sources and the PV photovoltaic sector has enormous development potential. The article's authors focused on one application criterion in technology development in the chosen area of the photovoltaic industry, item 3 of Table 1.

No	Application Criteria	Specific Tasks to Be Performed			
1	Absorber	Development of performed research on contaminati and technical defects of modules/panels Development of thinner and larger wafer areas for more efficient use Development of new passivation techniques			
2	Photovoltaic cells	Developing lower-cost manufacturing solar cells Designing high-precision equipment for accurate solar cell processing Improving anti-reflection layers and light-trapping in the solar cells			
3	Metal grids (contacts)	Reducing surface recombination by minimizing contact surfaces and strong doping under contacts			
4	Interconnection	Developing modern ways of joining solar cells			
5	Packaging	Innovative drive to reduce optical losses Developing changes in the appearance of modules Improving inspection systems to detect defects, automatically record their identified class, and reduce them while maintaining high sensitivity, efficiency, and process performance Developing new materials to reduce the cost of creating modules while maintaining their operational reliability			
6	Manufacturing	Ongoing innovation in commercially used products Introducing changes at every stage of production to improve the finished product			

Table 1. Technology development in various areas of the photovoltaic industry [4].

Production technologies and the application of surface layers have a stable position and are regarded as basic knowledge in the field of material engineering. Many research centers worldwide working on surface engineering are applying all possible means to describe the phenomena taking place on the surface of solids. Such a situation instigates scientists to undertake challenging research to determine the effect of conditions deposition of TCOs layers by various techniques and minimize electrical and optical losses occurring in functional layers of the entire ready electronic structure.

In light of the analysis of the literature review, the authors set out two new directions worthy of attention for further research. As new, experimentally obtained results in the temperature field of applying transparent conductive oxides on the contact metallization, one of the current research directions is the deposition of emitter conductive coatings, so layers of Transparent Conductive Oxides (TCOs) in photovoltaic structures by atomic layer deposition (ALD) [5].

On the other hand, the innovative nature of the research will concern the development of process engineering, which can include the presented dependence of the influence of lasermicro-machining on the improvement of the quality of the metallic component by minimizing the resistance of the connection of this front component with the substrate. Laser techniques are used in many areas of industry, including, among others, cutting, drilling, drawing, inspection and detection of quality defects in photo-elements, and shaping of material properties and structure [6]. Laser technology in producing photovoltaic cells with high efficiency in converting solar radiation into electricity is becoming an indispensable component of modern photovoltaic technology [7]. The components and functional layers of a silicon photovoltaic cell can include the layer forming the emitter of the solar cell, the passivation and anti-reflection layer, and the front and back electrodes [8,9].

According to the requirement of the EU Directive 2009/28/EC of the European Parliament and the Council, the increase in the use of renewable energy sources (RES) in the balance of final energy will be up to 20% in 2030. So the direction of the measures taken under this article is in line with the implementation of the Polish Energy Policy until 2030 [10].

2. Metal Grids

One of the current research topics in scientific units is the reduction of covering the front side of the cell by electrode contact paths, minimizing the so-called cover factor. In 2016, the width of the printed path of the front electrode was lower than 50 μ m, while the same in-line printing was reduced to a level below 20 μ m [11]. In 2031, it is expected that the width of the path will be reduced from 34 to 20 μ m, and overprint in line with greater precision will be reduced from 10 to 6 μ m. In 2021, the number of busbars in these solar cells was from 5 to 6, but in 2031 it will increase to more than 12 [11]. Figure 1 presents the market share of single- and double-sided solar cells. It is expected that from 2025 to 2025, the share of double-sided solar cells will prevail, although the share of single-sided solar cells will remain at about 40%.



Figure 1. The market dominance of single-double-sided contact concepts [3].

Figure 2 shows some estimations concerning reducing silver pastes/inks, the most expensive materials used in c-Si cell technologies. It is predicted during the following years to continue the reduction of silver per PV cell. In 2021 it was 80 mg for standard Passivated Emitter and Rear Contact (PERC), both single- and double-sided PV cells in the mentioned format in Figure 2. In 2031 we expected a reduction down to 50 mg per PV cell [3].



Figure 2. The trend for remaining silver per PV cell for chosen concept p-type (front and rear side of PV cell, where value for cell size are 166 and 166 mm²) [3].

The electrode application process must meet the requirements of, among others, industrial, such as high efficiency and low cost of production. It does not include photolithography, vacuum deposition techniques, and many chemical methods, as they involve

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too many manufacturing steps [12]. In practice, various industrial techniques can be applied to the front electrode [13]. The most common of these is the screen printing method, which is quick and straightforward and uses pastes based on silver and aluminium; it has been used since 1975 [14]. Since then, this method has evolved rapidly and has become the dominant technique in the photovoltaic industry. Yet the coating process of silicon layer using silk-screen printing is time-consuming and challenging to automate. The height adjustment of the coated layer necessitates the application of additional screens, which translates itself into additional costs. The mechanical load applied on the wafer/insert during electrode coating can bring about numerous cracks in it and other damage. Saving on the material through the recovery of its surplus as compared to other methods is impossible in this method since only pastes can be applied here instead of, for example, powders. Taking into account material factors and fabrication conditions (having an impact on quality, in particular with the application of pastes and powders) as well as economic factors, it seems to be grounded that further experimental research involving the initial phases of the process should be carried out [15–17].

Today, 95% of solar cells are metaled using this method. Compared to other methods, it is anticipated that the front electrode screening technique will remain the leading technique. In recent years, the design of screen printers has been improved, making it possible to produce more than 1500 cells per hour [18]. Lack of process repeatability with smaller path widths can significantly reduce the efficiency of solar cells by the influence of factors such as paste viscosity and clogging of the mesh or leaving traces of the screen mesh. It is assumed that forming metal contacts using the stencil printing technique is one of the most cost-effective solutions for producing high-efficiency solar cells [19].

In the case of a template, printing is easy. A template with a given shape is placed directly on the selected substrate, and, for example, the printed paste is pressed through the holes in the pattern with a squeegee (fabric, piece of wood). After removing the template, a printed pattern remains on the surface, representing the template [9,20]. We can be found in the literature the following printing methods: double print, which is known as print on print; the single print, which is understood as one screen print process for the whole metallization, as well dual print process, which is printed separately in two different printing processes both busbars and paths. Figure 3 shows predictions for using these methods for the deposit of silver pastes in the coming years. Although the share using the single print method will decrease, it will continue to have a significant market share. In comparison, the double print method will have a small impact on the market share of no more than 15%.



Figure 3. Prediction of the use of various front contact printing methods [3].

Compared to screen printing, new laser technology is quickly becoming one of the most promising and best alternative track application techniques. Laser technology in producing solar cells is becoming a necessary element of the modern, essential part of an automated operation in producing photovoltaic cells. Some examples involve the fabrication of front metallization using laser methods presented in available literature [16,21–23]. Solar cell technology is achieved using an advanced approach like selective emitter structures with the laser beam LDSE (Laser-doped Selective Emitter) [24]. More advanced solar cell

concepts include [25] metal or emitter wrap-through (MWT/EWT) [26,27], laser-fired contacts (LFC) [28] or interdigitated back contact (IBC) [29]. We can also find in the literature works on the optimization of metallization grids (for instance, the geometry) [30,31]. Of particular importance is the proper selection of the material of the electrode and substrate. Based on the data in [32], it is possible to find precisely 56 companies involved in the product of metallization paste, one of the essential supply items for PV cell producers. Based on Figure 4, we find information that the most significant number of companies producing silver paste (more than 60%) and the smallest number of copper paste (less than 8%).



Figure 4. Market survey on metallization pastes [32].

Currently, the photovoltaic market, specifically the part of the market responsible for pastes, is dynamically developing to help the customer and thus better adapt the offer to their expectations and requirements. Improving the efficiency of solar cells requires the application of low-temperature pastes in hetero-junction technology, manufacturing contact with emitters of high sheet resistance, reducing the consumption of paste applied for front and the rear connecting contacts, and applying advanced printing technologies (for example, dual printing is increasingly being implemented into production) [33].

3. Application of ALD and PVD Methods

The second of the current research directions is the deposition of conductive emitter coatings in photovoltaic structures using the ALD method, a variant of the CVD method [5]. The ALD process relies on the sequential release of the precursors in gaseous or liquid form to deposit the coating layer by layer. The first precursor is introduced into the reaction chamber, where it then forms a monolayer on the surface of the substrate. The chamber is then purged with an inert carrier gas (usually nitrogen or argon) to remove unreacted precursors and reaction by-products, and another precursor is introduced into the chamber to form another layer, followed by purging again [34]. The described phenomena are successive stages of one ALD cycle (Figure 5), and the entire coating process consists of many such cycles.



Figure 5. ALD cycle diagram.

Among the characteristic features of the ALD method are the sequentially of the process and the self-limiting rate of layer growth. The former is based on the fact that the

chemical precursors are introduced alternately into the growth chamber, and after each introduction of the reactant, the chamber is purged with an inert gas. Consequently, the combination of precursors occurs only at the surface of the substrate, unlike in the classical CVD method, where the reactants are introduced simultaneously, and the reactions between them occur in the gas phase. Thus, the ALD technique's layers are more homogeneous [35].

The coating application process consists of many cycles [34–38]. The ALD method can be used to deposit [36]:

- Single elements, e.g., from group IV of the periodic table,
- Binary compounds, e.g., metal oxides,
- Multi -component compounds, e.g., hydroxyapatite.

The precursors in the ALD process should have the following characteristics [39]:

- Volatility —gas pressure >0.1 Tr at <200 °C, liquid at evaporation temperature without decomposition,
- Reactivity —they can react quickly with the substrate and the other precursor in a self-limiting manner (most are air-sensitive),
- Stability -the precursor must retain physical and chemical properties at high temperatures,
- By -products-which should not react with the coating and be easy to remove from the reactor chamber,
- Availability at the lowest possible price.

In this process, it is easy to control the growth of the applied layer by controlling technological parameters such as, among others: substrate temperature, time of introducing precursor into the chamber, purging time after each reagent, the precursor temperature, and the number of cycles. The temperature is the most critical parameter that allows controlling the surface coverage directly. ALD processes occur at low temperatures below 350 °C [34,39,40]. The temperature range in which a saturation effect occurs with layer growth (one monolayer is formed in one cycle) depends on the ALD process in question and is referred to as the "ALD growth window". The temperature outside the "temperature window" generally results in poor growth rates and deposition of non-ALD layers due to low kinetics of the reactions taking place or too much condensation of the precursor on the substrate (at low temperature), or due to thermal decomposition or rapid desorption of the precursor (at high temperature). Schematically, the "growth window" is shown in Figure 6. To achieve the maximum benefits offered by the ALD method, it is crucial to realize the process within the limits of the characteristic "temperature window" [34,36].



Figure 6. Temperature dependence of layer growth rate [36].

The rate of chemical reactions in the ALD process, and thus the film growth rate, is strongly temperature-dependent and can vary in nature. Diagrams of the possible types of dependencies in the ALD window are shown in Figure 7 [40].



Figure 7. Dependence of growth rate on the temperature in the ALD window: (**a**) with increasing temperature, the growth rate decreases; (**b**) the growth rate is constant; (**c**) with increasing temperature, the growth rate increases; (**d**) the growth rate decreases with increasing temperature after reaching a maximum value [40].

Deposition of ALD thin films is carried out in specially adapted reactors. There are four different types of reactors [39]:

- With a closed chamber system,
- With an open chamber system,
- With a semi-closed chamber system,
- With a semi-open chamber system.

Currently, the most common type is a closed-chamber reactor. Layers are deposited in a growth chamber (reaction chamber), into which reactants are alternately introduced. Initially, they can be in the solid, liquid, or gas phase. The carrier gas in the process is an inert gas in whose atmosphere the deposition of layers takes place [39].

It can be stated, comparing them to the conventional coating application methods, that they has many advantages (Figure 8), including the possibility of using highly reactive precursors, homogeneity of the obtained layers and control of their thickness, and low surface roughness [39,41,42].



Figure 8. Comparison of ALD and CVD processes [39-41].

The main disadvantage of the ALD process is the limited range of materials that cannot be highly reactive and the selection of precursors characterized by low activation energy to prevent the thermo-degradation of the substrates [41]. The ALD process is time-consuming because the coating is created from many ultra-thin layers. The required thickness of the coating is obtained by repeating ALD cycles many times (even tens of thousands of times). The typical growth rate of the achieved layer is 100 to 300 nm per hour. Using specially designed reactors, it is possible to increase the deposition rate to $1-2 \mu m/h$. On the macroscopic scale, the process can be related to laminated coatings; however, the ALD process does not use adherents [41]. The coating materials used in the ALD process are extensive (Table 2), and the obtained layers may be [39]: single-element, two-component compounds, or multi-component compounds. Using ALD technology, it is possible to obtain mono-crystalline, polycrystalline, or amorphous layers.

Pure Elements	Oxides	Nitrides	Sulfides	Carbides	Fluoride
C, Al, Si, Ti, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Mo, Ru, Rh, Pd, Ag, Sb, Ta, W, Os, Ir, Pt	$\begin{array}{c} Al_2O_3, TiO_2,\\ Ta_2O_5, Nb_2O_5,\\ Zr O_2, HfO_2,\\ SiO_2, SnO_2,\\ In_2O_2, ZnO,\\ MgO, La_2O_3,\\ Y_2O_3, CeO_2,\\ Sc_2O_3, Cr_2O_3,\\ Er_2O_3, VO2,\\ B_2O_3, Co_2O_3,\\ CuO, Fe_2O_3,\\ NiO, Ga_2O_3,\\ WO_3, \ldots \end{array}$	AlN, TaNx, NbN, TiN, MoN, ZrN, HfN, GaN, WxN, InN, 	ZnS, SrS, CaS, PbS,	TiC, NbC, TaC,	CaF ₂ , SrF ₂ , ZnF ₂ ,

Table 2. Materials used to make ALD thin films [34,40,43].

4. Use of TCO in a Photovoltaic Structure

The third of the current research directions is related to transparent semiconductor oxides. For several years, this has been an exciting area of interest for many scientists and research centers [44]. These materials are of particular interest to the field of optoelectronics and photovoltaics [45]. This is confirmed by the report [46], which includes classifying common features of both domains (Figure 9a). These include aesthetics, consistency in their use worldwide, and increased efficiency of photovoltaic cells with the same average visible light transmittance. Figure 9b shows the high photoconversion efficiency of cells based on crystalline silicon and perovskite, which was 26.1% and 25.2%, respectively. The efficiency mentioned above exceeds 25%, and similar values are also observed in the research on transparent photovoltaics. In [47], we can also find that for a perovskite solar cell, the high conversion efficiency was 25.7%. Moreover, the highest lab efficiency in thin film technology is 23.4% for CIGS and 21.0% for CdTe solar cells.



Figure 9. The perspective of the development of transparent photovoltaics: (**a**) classification of features, (**b**) classification of photoconversion efficiency of cells [46].

In [47], we find information about record lab cell efficiency for mono-crystalline and multi-crystalline silicon wafer-based technology (26.7% and 24.4%). In 2040, it is predicted that passivated emitter and rear Cells (PERC) made from c-Si and PV cells with aluminium back surface field (BSF) will be among the most prevalent solar cells in mass production using thick-film technology, which is used to produce electronic devices/modules [47].

In the case of optical tests, transmittance should be taken into account when analyzing the efficiency of the photovoltaic conversion of a cell. The transmittance should be considered an essential parameter with the photovoltaic conversion efficiency since the efficiency changes with it. Electronically conductive transparent layers are generally obtained based on compounds of indium, tin and zinc doped with tin [48,49]. Indium Tin Oxide (ITO) and Aluminium-doped Zinc Oxide (AZO) will be used in this work; therefore, they will be discussed later. The high transparency of 85–90%, conductivity above 1000 S/cm, charge carrier density of $1 \cdot 10^{21}$ carriers/cm³, and mobility of 10–100 cm²/Vs are the essential beneficial properties of ITO commonly known in the literature [50–52]. The ITO is often used in organic electroluminescence devices (for instance, thin-film transparent electrodes of liquid crystal displays (LCDs) [49,53–57]. The commercially available ITO targets with different doping contents can be used for the ITO deposition at relatively low temperatures [54,58–60]. Al-doped zinc oxide is one of the various indium-free materials, which has been known as one of the most promising materials for replacing ITO in electronic devices, because of its abundance, non-toxicity, high conductivity, high transparency in the visible region, and low costs [61,62]. Zinc oxide (ZnO) thin film, due to its wide range of electrical and optical properties, has become a technologically important material. It has been doped with n-type dopants such as Al, In, Ga, Mg, and B to improve ZnO electrical conductivity, optical properties, and thermal stability by providing the extra electron [63]. AZO thin films have been fabricated by various techniques, such as atomic layer deposition and pulsed laser deposition [64], magnetron sputtering, chemical vapor deposition [65], and solution processing [66–69]. Fluorine-doped tin oxide (FTO) thin film has been used mainly for electronics devices making technologies, for instance, window layers in solar cells [70], gas sensor devices [71], substrates for electro-deposition [72], and transparent contact in optoelectronic and so on. For photovoltaic applications, TCO can be applied as front electrodes of thin film solar cells because of their excellent electrical properties $(4.3 \times 10^{-4} \text{ } \text{w.cm} 4.3 \times 10^{-4} \text{ } \text{w.cm})$ combined with high transmission properties (86%) [73]. The paper [74] presented a concept of preparing TCO nanocomposite by combining TCOs and nanoparticles. This example provides guidelines for designing hazy electrodes as light management structures in thin film photovoltaics. FTO is characterized in various technology fields because of its high electrical conductivity, chemical and thermal stability, and optical transparency in the visible range (74). For example, in paper [75], a sol-gel-spin-coating method was used to create a reproducible, scalable, stable, transparent, and conducting tin fluorine-doped indium oxide thin film (FTIO thin film). The method reduced sheet resistance by more than 53% ($\leq 7 \pm 1 \Omega/sq$) of the initial sheet resistance. Pulsed laser deposition [76], chemical vapor deposition (CVD) [77], and sol-gel and spray pyrolysis deposition (SPD) [78]—are just some of the methods used to prepare TCO [79]. Figure 10 shows an example of a PV structure and the use of TCO in this structure.



Figure 10. An example of a planar structure of a perovskite-based photovoltaic cell [1].

The issue of TCO was analyzed based on data from the Elsevier (Science Direct), Web of Science, and Scopus databases [80–82]. Based on Table 3, it can be concluded that the

Elsevier database recorded the highest number of published papers. The Scopus database was second, and WOS was third regarding issues analyzed (state of knowledge as of 7.09.22).

Table 3. List of issued publications on general topics according to three databases [80–82].

Issue Searched	Year		WOS	SCOPUS	ELSEVIER
Transparent Conductive Oxides	2012–2022	2382	814	4172	814

Table 4 summarizes the results of specific issues in the two databases, WOS and Scopus, as of 2020. Analyzing the results obtained, it can be concluded that a higher number of published papers related to issues related to SnO_2 is contained in the WOS database than in Scopus, while a comparable number of publications was found for the issue of "*AZO and* In_2O_3 " for both databases is contained in the WOS database and Scopus. The issue "FTO and In_2O_3 " contains the WOS database than Scopus (state of knowledge as of 5 April 2022).

Table 4. List of publications issued according to two databases with details [80,81].

WOS	SCOPUS	WOS	SCOPUS	WOS	SCOPUS	WOS	SCOPUS
AZO and In ₂ O ₃		FTO and In ₂ O ₃		In ₂ O ₃		TCO and In ₂ O ₃	
6	6	38	20	9.116	5.710	561	376
AZO and SnO ₂		FTO and SnO ₂		SnO ₂		TCO and SnO ₂	
22	36	1478	401	34.258	25.305	579	516

Some discrepancies in the scientific circulation of published research results in scientific journals in the aforementioned bibliographic databases may be due to the emergence of an increasing number of scientific journals that do not consider the low quality of non-scientific publications. Thanks to the development of information technology, bibliographic lists have been transferred to the virtual space, which has given them a new meaning [83].

5. Summary

External operating parameters characterizing electronic instruments (for example, open-circuit voltage (V_{oc}), short-circuit current (I_{sc}), filling factor (FF), and photovoltaic conversion efficiency (E_{ff}) are the values depending on the material and physical parameters of their separate layers and structural elements [84,85]. The elements and functional layers of an electronic device based on crystalline silicon (c-Si) include an impurity layer forming the emitter of the device, a passivating layer, an anti-reflective coating (ARC), and a front and rear electrode [78,85]. The electronic device's final operating parameters also determine the base material's parameters: the starting crystalline silicon wafer, the essential properties of resistivity and the lifetime of minority charge carriers. Consequently, only the mutual combination of the parameters of the base material, the parameters of the layers, and the functional elements of the instrument allows for obtaining an electronic device with the highest quantum efficiency value available for a given set of output parameters [78,85].

Production technologies and the application of surface layers have a stable position and are regarded as basic knowledge in the field of material engineering. In light of the analysis of the literature review, the authors set out two new directions worthy of attention for further research. Further work will require, as appropriate: determining the properties of thin TCO layers applied on silicon substrates by the ALD method for application as conductive emitter coatings in engineering structures, development of engineering structures based on silicon substrates with TCO layers and front contacts, development of a technology for applying a thin layer of TCO on a silicon substrate. According to the requirement of EU Directive 2009/28/EC of the European Parliament and the Council, the increase in the use of renewable energy sources (RES) in the final energy balance will be up to 20% in 2030. Thus, the direction of actions taken in the implementation doctorate is consistent with the implementation of the Polish Energy Policy until 2030 [10].

In sum, the implementation of significant achievements in the coming decade is in line with the fundamental guidelines for the development of photovoltaics as a result of [10,46,78] for the development of guidelines for metallization processes and TCO layers deposited by the ALD method.

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