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Structure and Properties of Thin Films Prepared on Flexible Substrates from SnCl_4 -Derived Solutions

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Abstract: Thin transparent films of SnO_2 were obtained from aqueous–alcohol solutions of SnCl_4 on a flexible polyethylene terephthalate (PET) substrate by spray pyrolysis at 100 °C. The influence of the addition of aqueous ammonia to the film-forming solution on the different properties has been studied. Properties studied include surface morphology, phase composition and transparency of the formed films and the crystallization processes and band gap of the film material. It was found that the addition of aqueous ammonia causes the formation of skeletal crystals $(\text{NH}_4)_2[\text{SnCl}_6]$ with a perovskite structure in the film structure. The resulting films are promising for use in the technology of manufacturing flexible solar cells.

Keywords: film-forming solutions; SnO_2 ; skeletal crystals; transparency; perovskite structure; band gap



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1. Introduction

Tin dioxide thin films have been of continuous interest to researchers since they have been successfully used in semiconductor electronics, optoelectronic devices, photonic systems, and power harvesting and storage devices [1–3]. In recent years, the development of highly efficient perovskite solar cells with a SnO_2 -conducting layer has become a promising research area [4–9].

Flexible perovskite solar cells (PSCs) as power sources have attracted much attention in mobile and portable electronics due to their high efficiency, excellent flexibility and relatively low cost. The durability, crystallinity and photovoltaic properties of each functional layer are essential for high-performance PSCs [4,8].

Typically, PSCs are multilayer devices with a sandwich structure consisting of an electron transport layer (ETL), a perovskite active layer, a hole transport layer (HTL), and a metal electrode [4,6].

The active layer of PSC is a metal halide perovskite compound that is used as a light absorber. The crystal structure of metal halide perovskites is the same type as calcium titanium oxide (CaTiO_3). Perovskite-like compounds have the general chemical formula ABX_3 , where “A” is the crystallographic site that represents monovalent cations such as organic methylammonium (CH_3NH_3) and formamidinium ($\text{CH}(\text{NH}_2)_2$) or inorganic cations such as cesium (Cs) and rubidium (Rb). “B” represents a heavy divalent metal such as lead (Pb) or tin (Sn), and “X” is a halogen anion (i.e., Cl^- , Br^- , I^-).

In the last decade, much attention has been paid to identifying potential cationic or anionic candidates that could be partially incorporated into perovskites to tune the

crystal chemistry, optoelectronic properties, photoconversion efficiency and stability of PSCs. Much effort has been directed towards the “A” and “X” sites since alternation at the “B” sites resulted in instability of the perovskite phase. Therefore, lead (Pb) has been the “B” site element of perovskites for many years. Selecting specific anions and cations at the “A” and “X” sites facilitated optimal tuning of the band gap, thereby bringing control to electrical and optical properties, such as increasing carrier transport distance and mobility as well as broadening the infrared absorption spectral range [4,10]. Lately, research efforts have begun to focus on replacing lead (Pb) with tin (Sn) in the “B” site, as the use of lead-based perovskite solar cells in large-scale applications poses environmental concerns [11,12].

Tin-based perovskite is a promising alternative to lead-based perovskite due to its environmental friendliness and superior optoelectronic properties. In particular, tin-based perovskite has a bandgap of 1.3–1.4 eV [13].

While preparing thin films of tin-based perovskite, scientists encountered rapid crystallization of perovskites, which often led to poor morphology and incomplete substrate coverage [14,15]. The morphology of tin perovskite thin films was improved by adding methyl ammonium chloride to the precursor solution [15].

SnO₂ films that can be prepared by spray pyrolysis have emerged as early candidates for the PSC electronic transport layer due to their simple fabrication process and superior performance [4]. Spray pyrolysis is a convenient, fast, and low-cost method for preparing thin films. With this method, films with a desired stoichiometric ratio can be easily deposited, and the film thickness can be controlled. Moreover, the films can be doped with various elements simply by adding them to the precursor solution for further sputtering. Also, this method can be easily scaled up to prepare large-area films [16,17]. This method allows one to regulate the temperature of the substrate during the deposition of the SnO₂ film on it or the temperature of the subsequent short-term processing of the films [17,18].

The purpose of this work was to obtain thin SnO₂ films by spray pyrolysis on a flexible substrate from aqueous–alcohol solutions of SnCl₄ and to study the crystal structure and optical properties of the resulting films using aqueous ammonium in a film-forming solution as an initiator for the formation of perovskite crystals in the structure of thin films.

2. Materials and Methods

2.1. Preparation of Thin Films on Flexible Polyethylene Terephthalate Substrates

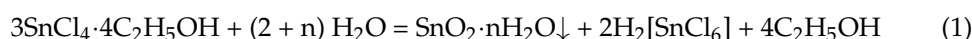
Thin films were coated on polyethylene terephthalate (PET) substrates using spray pyrolysis from 0.11 molar tin tetrachloride solutions with and without ammonium hydroxide.

2.1.1. Procedure for Preparing SnCl₄ Solutions

Two variants of tin tetrachloride solutions were used for the preparation of the films: “SnCl₄ in ethanol” and “SnCl₄ in ethanol with the addition of an aqueous solution of ammonia NH₃·H₂O”. Tin tetrachloride crystal hydrate (SnCl₄·5H₂O “pure”) was preliminarily ground manually in a mortar to a powdered state.

To prepare a 0.11 molar solution of “SnCl₄ in ethanol” (No. 1), weighed quantity 3.9072 g of crushed SnCl₄·5H₂O was used, which was dissolved in 100 mL of rectified ethyl alcohol (Russian State Standard–GOST 5962-13). Tin (IV) chloride is a strong complexing agent [19]. When dissolving tin (IV) crystal hydrate in ethanol, the reactants interact to form the chemical compound SnCl₄·4C₂H₅OH, which can be represented as a complex compound, which is the electrolyte [Sn(C₂H₅OH)Cl₂]₂ [20].

Since water is present in the crystal hydrate (as well as in rectified ethanol), it can be assumed that SnCl₄ undergoes hydrolysis with the formation of tin oxide hydrate SnO₂·nH₂O (where n = 1 ÷ 2) and hexachlorostannic acid H₂[SnCl₆] [19]. In our case



The observed gel-like precipitate is associated with the formation of tin oxide hydrate SnO₂·nH₂O (n = 1 ÷ 2), i.e., stannous acid [19]. Initially α-stannous acid is formed, which

can either dissolve in an acidic medium or, as it ages, transform into β -stannous acid as a result of oxolation, as Figure 1.

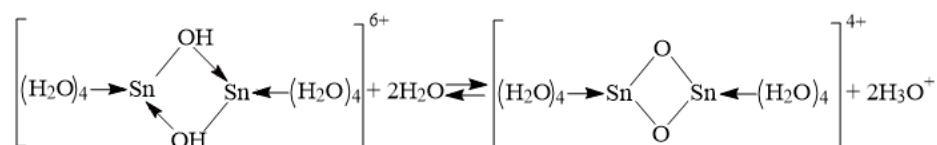


Figure 1. α -stannous acid.

β -stannous acid does not dissolve in the acidic medium of the solution but is peptized by it. Further, as it ages, the oxol bridge groups are connected to each other, as Figure 2. This leads to the enlargement of the formed particles [19].

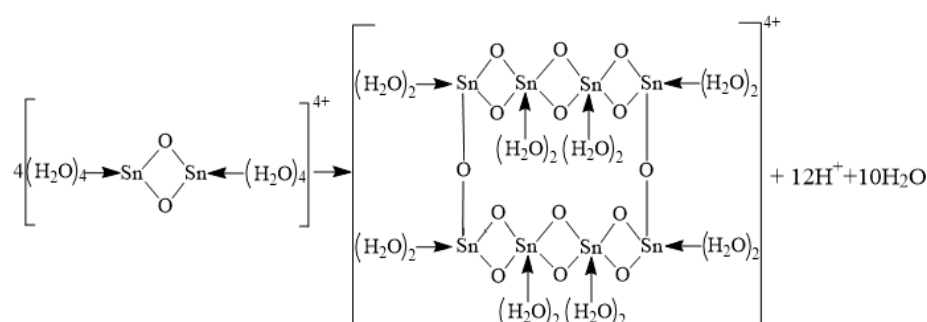
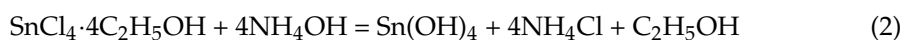


Figure 2. β -stannous acid.

Thus, it is the formation of polysolvated and oxol structures in aqueous–alcoholic solutions of SnCl_4 that provides their film-forming properties and the possibility of forming SnO_2 films.

“ SnCl_4 solution in ethanol with addition of aqueous ammonia solution” (No. 2) was prepared as follows. A weighed quantity of 3.9072 g of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ was dissolved in 50 mL of ethanol with continuous stirring. Then, 1 mL of concentrated (25 wt. %) aqueous ammonia solution was added, which is ammonium hydroxide NH_4OH , which is in equilibrium with ammonia ($\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_3 \cdot \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^-$). NH_4OH is highly soluble in ethanol, and in the absence of a catalyst, chemical interaction between these reagents is unlikely [21].

When ammonium hydroxide was added to the solution “ SnCl_4 in ethanol”, the formation of a white gelatinous precipitate of tin hydroxide was observed:



At the same time, the previously formed hexachlorostannic acid can react with ammonium hydroxide to form ammonium hexachlorostannate:



Next, ethanol was added to this solution until the volume of the resulting solution was 100 mL. The resulting solution, “ SnCl_4 solution with the addition of an aqueous ammonia solution” (No. 2), was placed in a dark place for 1 day to mature. After that, it became transparent.

2.1.2. Film Formation Procedure

The films were coated to flexible substrates—polyethylene terephthalate (PET) plates measuring $4 \text{ cm} \times 7 \text{ cm} \times 14 \text{ }\mu\text{m}$. The surface of the plates was cleaned using a mild detergent (Fairy soap), followed by rinsing with running and distilled water. The films

were coated to the substrates by spray pyrolysis. The gas pressure in the compressor for applying solutions was 50 kPa. The distance between the substrate and the sprayer was 32 cm. The solution was applied to the substrate heated to 100 °C. Then, the samples were annealed on an electric hotplate at 100 °C for 15 min.

2.2. Research Methods

The analysis of the surface morphology of the resulting films was carried out using an MPE-11 LOMO optical microscope.

The substrate thickness was measured using an MCC digital micrometer (in-Tool).

The phase composition of the obtained thin films was studied by XRD diffraction using Rigaku MiniFlex600. The crystallite sizes were calculated using the Scherer formula [22].

The band gap of the prepared films was calculated using the transmission and absorption spectra, which were obtained using a UNICO VV/VIS 2800 single-beam spectrophotometer in the spectral range of 190–1100 nm.

The thickness of the films was determined from the interference pattern in the transmission spectra. Mathematically, the condition for the appearance of interference peaks is described by the following equations [23]

$$\text{For the minimum : } 2dn_1\sqrt{n_2^2 - \sin^2\alpha} = m\lambda$$

$$\text{For the maximum : } 2dn_1\sqrt{n_2^2 - \sin^2\alpha} = (2m - 1)\frac{\lambda}{2}.$$

where d is the film thickness, n_1 is the refractive index of air, n_2 is the refractive index of the medium, α is the angle of incidence of the electromagnetic wave, m is the number of interference extremum, λ is the wavelength of electromagnetic radiation.

Since, in our case, the beam was directed perpendicular to the surface, the angle $\alpha = 0^\circ \Rightarrow \sin^2\alpha = 0$, whereas the refractive index of air is taken as 1 ($n_1 = 1$); then, for the minimum, $2dn_2 = m\lambda$, and for the maximum, $2dn_2 = (2m - 1)\frac{\lambda}{2}$. Accordingly, the wavelength at which the minimum is observed is $\lambda_{min} = (2dn_2)/m$, and the wavelength at which the maximum is observed is equal to $\lambda_{max} = \frac{4dn_2}{2m-1}$.

Mathematical modeling of interference peaks was carried out using Microsoft Excel. The position of the extrema was modeled depending on the film thickness. The refractive index of PET for the visible spectrum is taken to be $n = 1.64$, according to [24]. Wavelength calculations were carried out for extrema with serial numbers (m) from 1 to 100. The value of the transmittance coefficients for the maxima and minima was chosen arbitrarily, depending on the analyzed spectrum. By changing the film thickness values, the matching of mathematical peaks with experimental ones was achieved. The value of the film thickness at which the largest number of calculated extrema coincides with the experimental ones was taken as a solution.

To correctly determine the band gap of a transparent film coated on a transparent substrate, the absorption spectra of the substrate were subtracted from the absorption spectra of the samples. The band gap was determined by the Tauc method [25–27].

The method is based on the equation $(\alpha h\nu)^n = A(h\nu - E_g)$, where α is the optical absorption coefficient, cm^{-1} ; h is Planck's constant (4.136×10^{-15} eV·s); ν is the frequency of electromagnetic oscillations in the optical range, s^{-1} ; n is the exponent, which depends on the band structure of the semiconductor (for direct-band $n = 2$, for indirect-band $n = 1/2$); A is a constant which depends on the effective mass of charge carriers in the material; E_g is the width of the band gap of the semiconductor, eV.

3. Results and Discussion

According to the optical and SEM images of the surface of thin films presented in Figure 3, it is possible to evaluate the effect of the addition of ammonium hydroxide on the surface morphology of films formed on a flexible PET substrate.

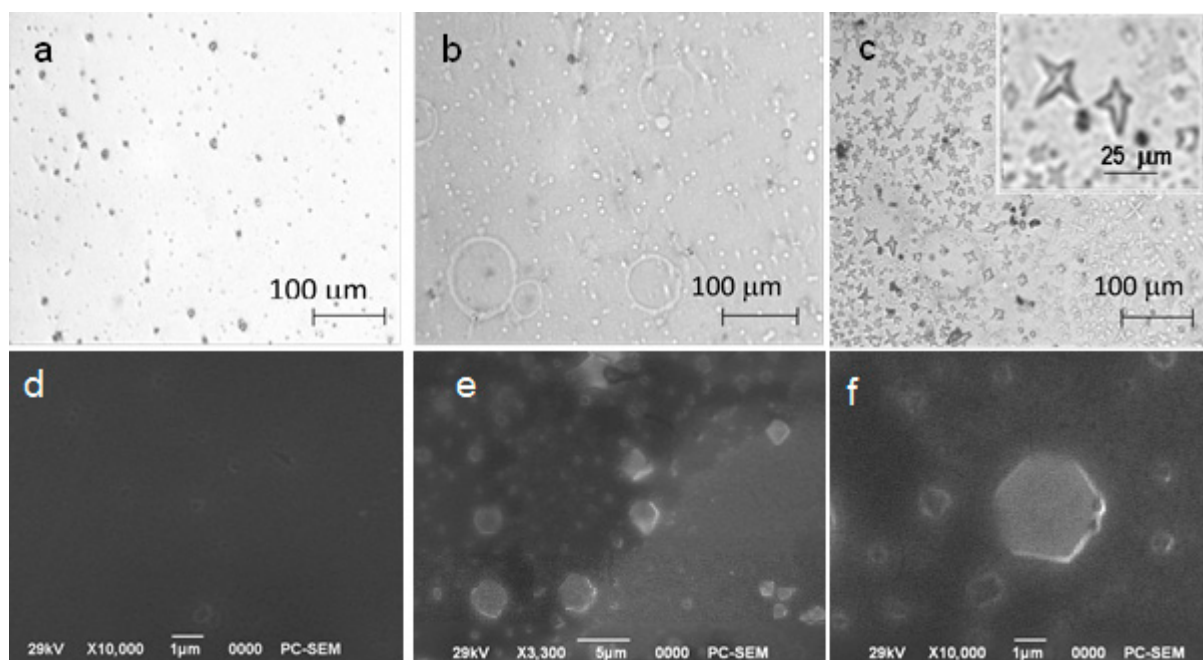


Figure 3. Optical and SEM images of the surface of a polyethylene terephthalate (PET) plate (a) and PET plates coated with films obtained from solutions No. 1 “SnCl₄ in ethanol” (b) and No. 2 “SnCl₄ in ethanol with the addition of NH₄OH” (c), SEM images of PET plates coated with films obtained from solutions No. 1 “SnCl₄ in ethanol” at 10,000× magnification (d), PET plates coated with films obtained from solutions No. 2 “SnCl₄ in ethanol with the addition of NH₄OH” at 3300× magnification and (e) 10,000× magnification (f).

As can be seen from Figure 3b,f, a solid homogeneous film is formed from solution No. 1 “SnCl₄ in ethanol”. Only isolated drop-shaped stains are observed due to the coating method. Thus, solution No. 1, “SnCl₄ in ethanol”, can be considered film-forming.

A continuous film is also formed from solution No. 2, “SnCl₄ in ethanol with the addition of NH₄OH”; Figure 3c. However, skeletal crystals are formed on the surface of this film. These crystals are characteristic of the coatings obtained from film-forming solutions of inorganic compounds [28–30]. At 3300× magnification, Figure 3e, and 10,000× magnification, Figure 3f, it can be seen that the film consists of crystals of predominantly hexagonal shapes of various sizes.

To determine the composition of the resulting films, an X-ray phase analysis was carried out (Figure 4).

It can be seen that the X-ray diffraction pattern for the PET substrate without coating (Figure 4a) contains two reflections at $2\theta = 25.92^\circ$ and one less pronounced one at 53.58° . The X-ray diffraction pattern of PET with a film obtained from solution No. 1 without NH₄OH (Figure 4b) does not show new reflections associated with reflection from crystalline structures in the film. So, the structure of the film obtained from solution No.1, “SnCl₄ in ethanol”, can be considered amorphous. This is also confirmed by literature data, which state that amorphous films of SnO₂ are formed from solutions based on SnCl₄ up to a temperature of 300 °C, and after 300 °C, SnO₂ crystals grow mainly in the (200) direction [31].

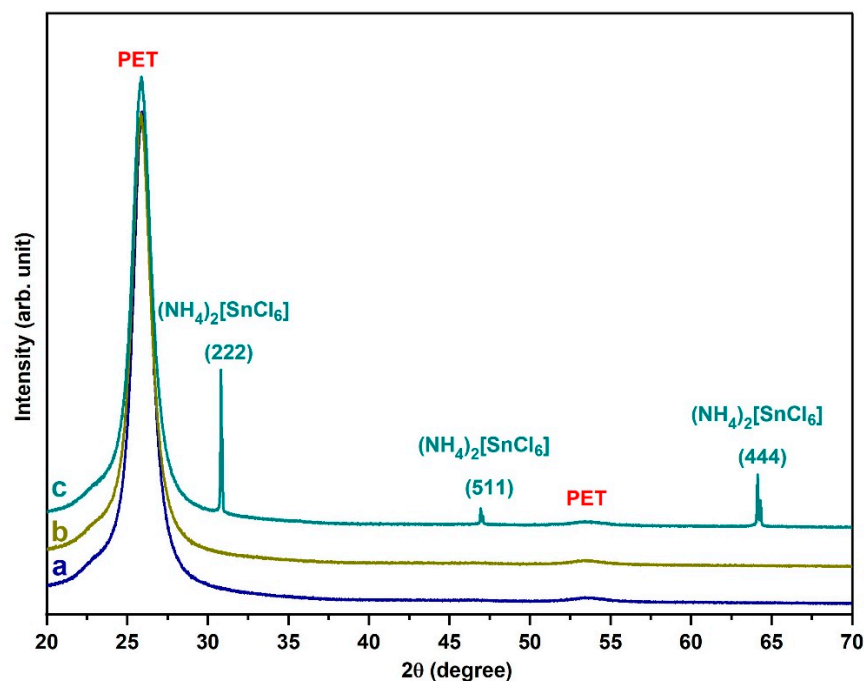


Figure 4. X-ray diffraction patterns of a polyethylene terephthalate (PET) plate (a) and PET plates coated with films obtained from solutions No. 1 “SnCl₄ in ethanol” (b) and No. 2 “SnCl₄ in ethanol with the addition of NH₄OH” (c).

Film obtained from film-forming solution No. 2, “SnCl₄ in ethanol with the addition of NH₄OH” (Figure 4c), demonstrates diffraction peaks from the crystalline phase of the complex compound (NH₄)₂[SnCl₆]. The crystallinity of the phase is 97.8(5)%. The possibility of the appearance of precise crystals of ammonium hexachlorostannate (IV) is confirmed by the abovementioned analysis of the chemical processes occurring in film-forming aqueous–alcohol solutions of SnCl₄ when ammonium hydroxide is introduced into them (see Section 2.1.1, Equation (3)). The formation of crystals of exactly this phase composition (NH₄)₂[SnCl₆] is associated, first of all, with the technique of coating film-forming solutions by spray pyrolysis with a low-heat treatment temperature. SnO₂ crystals are formed when film is coated by spin-coating followed by annealing, usually at a higher temperature [32–34]. The obtained ammonium hexachlorostannate (IV) (Pink’s salt) is an inorganic complex compound of tin chloride and ammonia. Ammonium hexachlorostannate (IV) (NH₄)₂[SnCl₆] forms colorless crystals of a cubic system, space group F m3m, with cell parameters $a = 1.0058$ nm, $Z = 4$ [35].

The results of the crystallite size calculations are presented in Table 1, where 2θ is the X-ray reflection angle; hkl are crystallographic planes; d is the crystallite size.

Table 1. Calculated crystallite sizes for (NH₄)₂[SnCl₆].

2θ	hkl	d , nm
30.8190	2 2 2	111
46.94	5 1 1	89
64.1304	4 4 4	205
83.18	7 5 1	169

The sizes of the formed (NH₄)₂[SnCl₆] crystallites (Table 1) vary from ~90 nm in the direction of the (511) crystallographic plane to ~200 nm in the (444) direction.

Ammonium hexachlorostannate (IV) has a perovskite structure [35,36]. Perovskites have excellent optoelectronic properties and have broad prospects for use in photodetectors, LEDs, and solar cells [37–39].

So, the XRD results showed that skeletal crystals of $(\text{NH}_4)_2[\text{SnCl}_6]$ formed in the film-coated from solution No. 2, “ SnCl_4 in ethanol with the addition of NH_4OH ”. The amorphous base of the films is formed by tin (IV) oxide that did not crystallize at low-heat treatment temperatures ($100\text{ }^\circ\text{C}$) for both solutions: No. 1, “ SnCl_4 in ethanol”, and No. 2, “ SnCl_4 in ethanol with the addition of NH_4OH ”.

To further study the composition of the films and their optical properties, their optical spectra were taken. Calculation of the band gap of the compounds formed in thin films obtained from solutions No. 1 and No. 2 made it possible to indirectly estimate the composition of these films.

Figure 5 shows the transmission spectra of a pure PET substrate and PET with coated thin films.

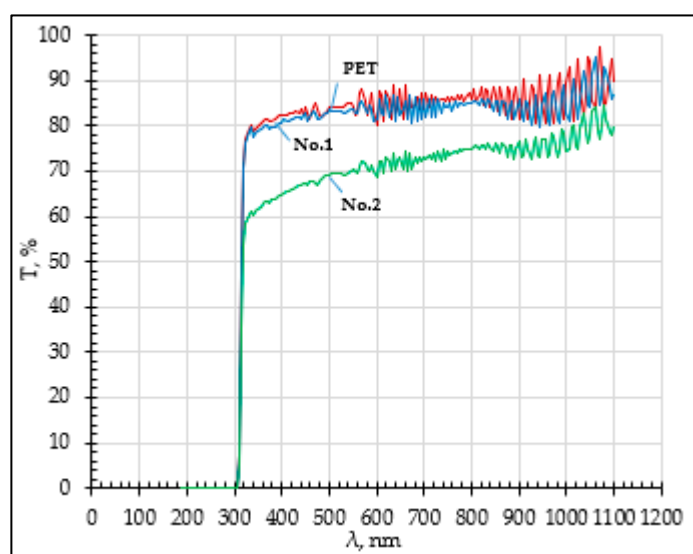


Figure 5. Transmission spectra taken from a PET substrate without film and with films obtained from solutions No. 1, “ SnCl_4 in ethanol”, and No. 2, “ SnCl_4 in ethanol with the addition of NH_4OH ”.

The pure PET substrate (Figure 5) has a transmittance of 81–97% in the wavelength range of 350–1100 nm. The PET substrate with a thin amorphous film deposited from solution No. 1 has a transmittance of ~79–95%. The PET substrate with a film with precipitated $(\text{NH}_4)_2[\text{SnCl}_6]$ crystals obtained from solution No. 2 has a transmittance of ~61–85%. Thus, both coating of a film with a homogeneous structure and a film with crystalline inclusions on a PET substrate expectedly reduces the transmittance in both cases. However, the transmittance remains quite high, which is an important factor for further practical application of the resulting thin films.

Interference peaks are observed in the transmission spectra of all samples (Figure 5). The results of the mathematical modeling of the interference peaks for a pure PET substrate are shown in Figure 6a. The height of the simulated peaks is taken arbitrarily. As can be seen from Figure 6a, the calculated interference peaks coincide quite well with the experimental ones from the maximum observed at a wavelength of 585 nm to the maximum at 1090 nm. The match occurs from the maximum $m_{\text{max}} = 76$ to $m_{\text{max}} = 41$ at $d = 14,000\text{ nm}$. That is, the thickness of the PET substrate is $14\text{ }\mu\text{m}$, which corresponds to direct measurements of the thickness of the substrate (Table 2).

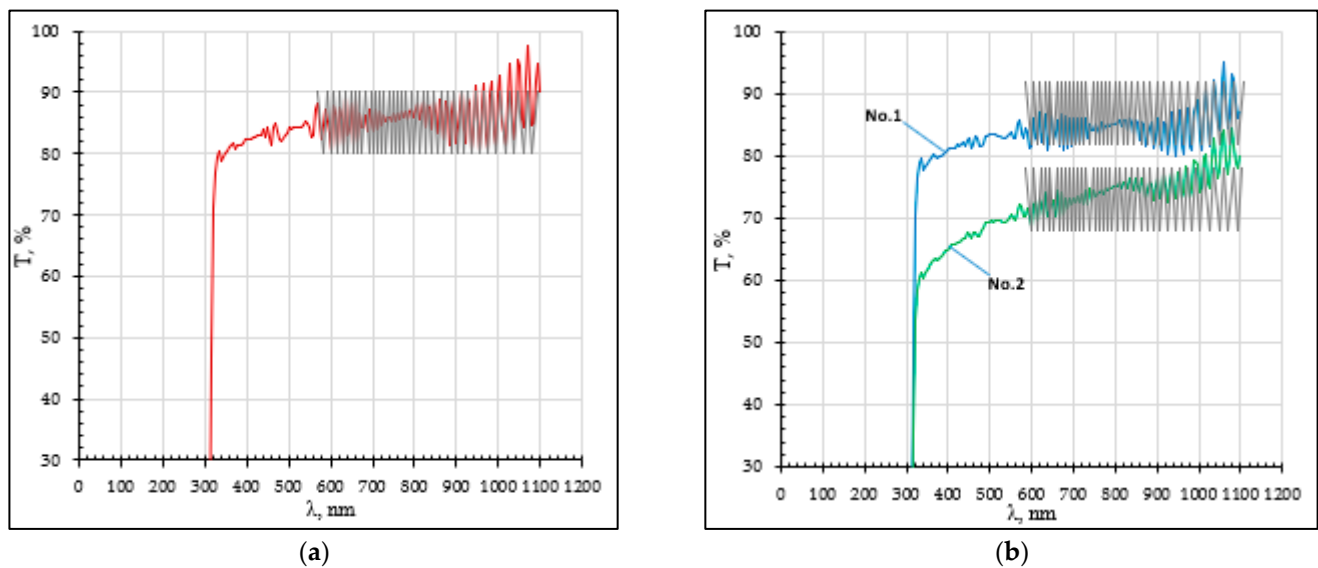


Figure 6. Transmission spectra from a PET substrate without films (a) and with films No. 1 and No. 2. (b) with the results of mathematical modeling of interference peaks (gray lines).

Table 2. Comparative properties of the studied thin films obtained from solutions No. 1, “SnCl₄ in ethanol”, and No. 2, “SnCl₄ in ethanol with the addition of NH₄OH”.

Object	Thickness	Transmittance $\lambda = 350\text{--}1100\text{ nm}$ %	Bandgap, eV		Film Structure and Composition
			Experimental Values	Literature Data	
PET substrate	14 μm	81–97%	3.98	3.94 [40,41] 3.9 [42]	—
Film from solution No. 1	100 $\pm$ 5 nm	79–95	4.04	4.05 and 4.10 [43] 3.9–4.2 [44]	amorphous matrix of SnO ₂
Film from solution No. 2	120 $\pm$ 5 nm	61–85	2.64	2.7 [45]	SnO ₂ matrix with skeletal crystals (NH ₄) ₂ [SnCl ₆] ~90–200 nm

Interference peaks are also observed in the spectra of the PET substrate with coated films (Figure 5). The appearance of interference peaks corresponds to the presence of the PET substrate. However, the interference peaks for the pure PET substrate and the substrate with No. 1 and No. 2 are not identical. These discrepancies are caused by the increase in thickness due to the films’ coating. In this regard, calculations were carried out for the transmission spectra for the PET substrate with films No. 1 and No. 2. The graphical results are presented in Figure 6b.

Thickness calculations were carried out for extrema from the 1st to 100th orders. Figure 6 shows extrema from orders 75th to 41st (gray curves) since these extrema are clearly expressed in the experimental curves. It is difficult to visually assess the shift of the extremes. Therefore, changes in the position of the extremum depending on the thickness of the sample are presented using the example of extrema of the 47th and 48th order in Table 3.

Table 3. Position of extrema depending on sample thickness.

Object	Thickness (<i>d</i>), nm	Serial Number of Interference Extremum (<i>m</i>)	Wavelength at Which the Extremum Is Observed (λ), nm	
			λ_{max}	λ_{min}
PET substrate	$14,000 \pm 5$	47	987.5	977.0
		48	966.7	956.7
Film from solution No. 1	$14,100 \pm 5$	47	955.8	945.6
		48	935.6	925.9
Film from solution No. 2	$14,120 \pm 5$	47	957.1	946.9
		48	936.9	927.2

According to calculations (Table 3), the increase in the thickness of the samples was 100 ± 5 nm for a film with an amorphous homogeneous structure obtained from solution No. 1 and 120 ± 5 nm for a film with crystalline inclusions from solution No. 2. These values can be taken as the thickness of the coated films (Table 2).

Figure 7 shows Tauck plots meant to determine the band gap.

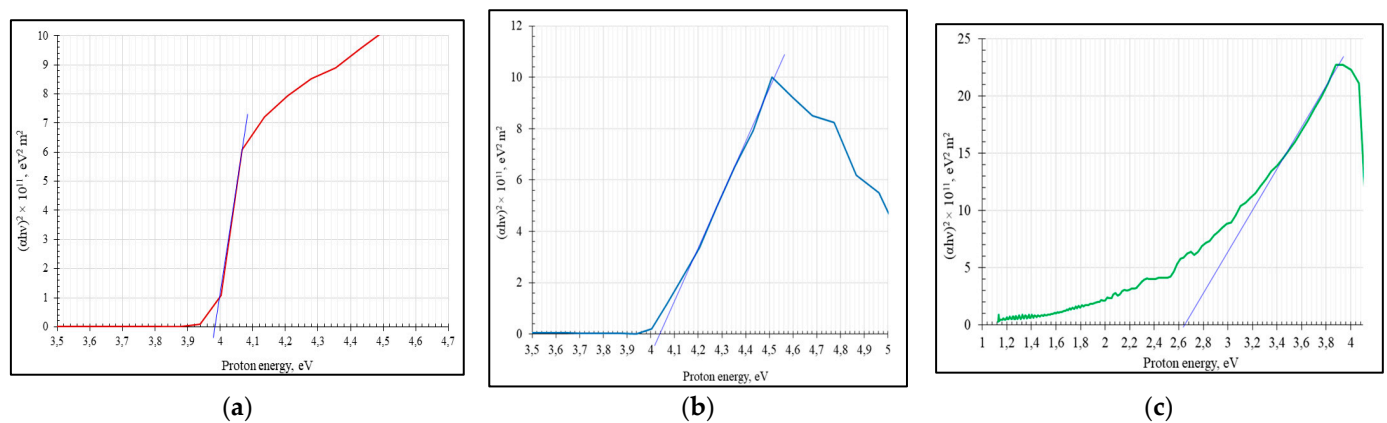


Figure 7. Illustration of the graphical determination of the band gap for a PET substrate without film (a), with film No.1 being homogeneous in structure (b) and film No. 2 containing crystalline inclusions $(\text{NH}_4)_2[\text{SnCl}_6]$ (c).

Figure 7a shows that the band gap for the polyethylene terephthalate substrate is 3.98 eV. This is consistent with the literature data [40] and indicates that the method for determining the band gap is correct.

The band gap of the film obtained from solution No. 1, “ SnCl_4 in ethanol”, is 4.04 eV (Figure 7b), which can vary from 3.5 eV to 4.5 eV for SnO_2 depending on the method of preparation according to the literature data [46,47]. According to our previous studies, the band gap of SnO_2 thin films coated using a film-forming system of the same composition by dipping is exactly 4.05–4.1 eV [33,43]. Thus, our assumptions regarding the phase composition of the amorphous SnO_2 film are confirmed by the obtained value of the band gap.

The band gap of the film obtained from solution No. 2, “ SnCl_4 in ethanol with the addition of NH_4OH ”, is 2.64 eV (Figure 7c). This band gap does not correspond to the band gap of SnO_2 . The presence of $(\text{NH}_4)_2[\text{SnCl}_6]$ crystals in the film led to a decrease in the band gap from 4.04 to 2.64 eV. This may have a beneficial effect on the further use of these films in electronic devices, particularly in increasing the efficiency of perovskite solar cells.

Solar cells can be either multi-component [48,49] or consist of two cells—the upper and lower solar cells—which act as diode absorbers [50]. The maximum energy conversion efficiency can be achieved if the band gap of the upper diode is $E_{g_{top}} = 0.5 \times E_{g_{bot}} + 1.15$ eV.,

where $E_{g\text{top}}$ and $E_{g\text{bot}}$ are the band gaps of the upper and lower diode absorbers [51]. Most often, crystalline silicon with a band gap of 1.15 eV is used as the lower diode. Therefore, the ideal band gap of the upper diode is ~ 1.725 eV. That is, reducing the band gap from 4.04 to 2.64 eV will increase the energy conversion efficiency of a two-component solar cell.

4. Conclusions

Continuous thin transparent films with a thickness of ~ 100 – 120 nm were obtained on a flexible transparent polyethylene terephthalate substrate using low-temperature spray pyrolysis from film-forming aqueous–alcohol solutions based on SnCl_4 . It has been established that when an aqueous solution of ammonia is added to these solutions, films with the inclusion of $(\text{NH}_4)_2[\text{SnCl}_6]$ skeletal crystals with a perovskite structure were formed instead of amorphous SnO_2 films formed at 100°C . The phase composition of the resulting films was confirmed by X-ray diffraction and bandgap calculations. The inclusion of $(\text{NH}_4)_2[\text{SnCl}_6]$ crystals into the SnO_2 film led to a decrease in the band gap of the film material from 4.04 to 2.64 eV, which may have a beneficial effect on the further use of these films in electronic devices. Thin transparent SnO_2 films with inclusions of crystals with a perovskite structure are promising for use in flexible solar cells.

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References

1. Cobianu, C.; Savaniu, C.; Siciliano, P.; Capone, S.; Utriainen, M.; Niinisto, L. SnO_2 sol–gel derived thin films for integrated gas sensors. *Sens. Actuators B Chem.* **2001**, *77*, 496–502. [\[CrossRef\]](#)
2. Zur, L.; Tran, L.T.; Meneghetti, M.; Ferrari, M. Sol-Gel-Derived SnO_2 -Based Photonic Systems. In *Handbook of Sol-Gel Science and Technology*; Klein, L., Aparicio, M., Jitianu, A., Eds.; Springer: Cham, Switzerland, 2016; pp. 2301–2319. [\[CrossRef\]](#)
3. Dalapati, G.K.; Sharma, H.; Guchhait, A.; Chakrabarty, N.; Bamola, P.; Liu, Q.; Saianand, G.; Krishna, A.M.S.; Mukhopadhyay, S.; Dey, A.; et al. Tin oxide for optoelectronic, photovoltaic and energy storage devices: A review. *J. Mater. Chem. A* **2021**, *9*, 16621–16684. [\[CrossRef\]](#)
4. Tang, J.; Chen, Y.; Xu, Z.; Li, X.; Liu, M.; Chen, Z.; Zhang, P.; Li, S. Composites electron transport layer of PVA-regulated SnO_2 for high-efficiency stable perovskite solar cells. *J. Alloys Compd.* **2024**, *1004*, 175939. [\[CrossRef\]](#)
5. Riaz, S.; Min, L.; Zhenwu, Z.; Ying, Q.; Peng, W.; Cheng, J.; Ko, M.J.; Hongyu, M.; Qureshi, M.S.; Umar, S.; et al. Interfacial engineering and defect passivation of SnO_2 through agmatine sulfate in carbon-based perovskite solar cells. *Ceram. Int.* **2024**, *50*, 43550–43562. [\[CrossRef\]](#)
6. Panyathip, R.; Sucharitakul, S.; Hongsith, K.; Bumrungsan, W.; Yarangsi, V.; Phaduangdhitidhada, S.; Chanlek, N.; Choopun, S. Surface modification of SnO_2 electron transporting layer by graphene quantum dots for performance and stability improvement of perovskite solar cells. *Ceram. Int.* **2024**, *50*, 34840–34848. [\[CrossRef\]](#)
7. Zhou, Y.; Cao, J.; Chen, S.; Lu, Y.; Xu, J.; Xu, S.; Zhang, Y.; Zhang, X.; Wang, Z.; Sun, G.; et al. Multifunctional buried interface engineering via phenyl-phosphonic acid for efficient and stable SnO_2 -based planar perovskite solar cells. *Colloids Surf. A Physicochem. Eng. Asp.* **2024**, *702*, 135205. [\[CrossRef\]](#)
8. Lv, H.; Sun, Q.; Zhao, J.; Zhang, C.; Hao, Y.; Qin, W. Collaboration of SnO_2 :PAN NWs and BABr enable high-performance flexible perovskite solar cells. *Chem. Eng. J.* **2024**, *496*, 153945. [\[CrossRef\]](#)
9. Chen, L.; Li, X.; Zhang, N.; Yu, L.; Liu, Z.; Liu, H.; Song, G. Non-ionic polymeric polyacrylamide (PAM) modified SnO_2 electron transport layer for high-efficiency perovskite solar cells. *Sol. Energy Mater. Sol. Cells* **2024**, *272*, 112907. [\[CrossRef\]](#)
10. Yang, Y.; Hoang, M.T.; Bhardwaj, A.; Wilhelm, M.; Mathur, S.; Wang, H. Perovskite solar cells based self-charging power packs: Fundamentals, applications and challenges. *Nano Energy* **2022**, *94*, 106910. [\[CrossRef\]](#)

11. Espinosa, N.; Serrano-Luján, L.; Urbina, A.; Krebs, F.C. Solution and vapour deposited lead perovskite solar cells: Ecotoxicity from a life cycle assessment perspective. *Sol. Energy Mater. Sol. Cells* **2015**, *137*, 303–310. [\[CrossRef\]](#)
12. Zhang, J.; Gao, X.; Deng, Y.; Li, B.; Yuan, C. Life Cycle Assessment of Titania Perovskite Solar Cell Technology for Sustainable Design and Manufacturing. *ChemSusChem* **2015**, *8*, 3882–3891. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Wang, T.; Cao, J.; Yan, F. Optimization of interface property in tin-based perovskite solar cells. *Matter* **2024**, *7*, 2755–2757. [\[CrossRef\]](#)
14. Liu, J.; Ozaki, M.; Yakumaru, S.; Handa, T.; Nishikubo, R.; Kanemitsu, Y.; Saeki, A.; Murata, Y.; Murdey, R.; Wakamiya, A. Lead-Free Solar Cells based on Tin Halide Perovskite Films with High Coverage and Improved Aggregation. *Angew. Chem. Int. Ed.* **2018**, *57*, 13221–13225. [\[CrossRef\]](#) [\[PubMed\]](#)
15. Cuzzupè, D.T.; Öz, S.D.; Ling, J.K.; Illing, E.; Seewald, T.; Jose, R.; Olthof, S.; Fakharuddin, A.; Schmidt-Mende, L. Understanding the Methylammonium Chloride-Assisted Crystallization for Improved Performance of Lead-Free Tin Perovskite Solar Cells. *Solar RRL* **2023**, *7*, 24. [\[CrossRef\]](#)
16. Li, M.; Zhao, L.; Guo, L. Preparation and photoelectrochemical study of BiVO₄ thin films deposited by ultrasonic spray pyrolysis. *Int. J. Hydrogen Energy* **2010**, *35*, 7127–7133. [\[CrossRef\]](#)
17. Hind, P.A.; Kumar, P.; Goutam, U.K.; Rajendra, B.V. Impact of deposition temperature on persistent photoconductivity of SnO₂ thin films deposited using spray pyrolysis technique suitable in optoelectronic synaptic devices. *Opt. Mater.* **2024**, *153*, 115579. [\[CrossRef\]](#)
18. Gunes, I.; Sarica, E.; Ozcan, H.B.; Terlemozoglu, M.; Akyuz, I. Flow rate-dependent properties of SnO₂ thin films deposited by ultrasonic spray pyrolysis. *Opt. Mater.* **2024**, *150*, 115189. [\[CrossRef\]](#)
19. Tretyakov, Y.D.; Martynenko, L.I.; Grigor'ev, A.N.; Tsivadze, A.Y. Inorganic Chemistry. In *Chemistry of Elements*, 2nd ed.; Moscow State University Publishing House Akademkniga: Moscow, Russia, 2007; Volume 2, 670p. (In Russian)
20. Rogov, S.V. Study of Interaction of Tin Chloride with Ethanol. Author's Abstract of the Ph.D. Thesis. Ph.D. Thesis, Leningrad Pedagogical Institute named after A.I. Herzen, Leningrad, USSR, 1955; 12p. (In Russian)
21. Klyuev, M.V.; Khidekel', M.L. Catalytic amination of alcohols, aldehydes, and ketones. *Rus. Chem. Rev.* **1980**, *49*, 14–27.
22. Konan, F.K.; Hartiti, B.; Batan, A.; Aka, B. X-ray diffraction, XPS, and Raman spectroscopy of coated ZnO:Al (1–7 at.%) nanoparticles. *E J. Surf. Sci. Nanotechnol.* **2019**, *17*, 163–168. [\[CrossRef\]](#)
23. Bonal, V.; Quintana, J.A.; Villalvilla, J.M.; Muñoz-Mármol, R.; Mira-Martínez, J.C.; Boj, P.G.; Cruz, M.E.; Castro, Y.; Díaz-García, M.A. Simultaneous Determination of Refractive Index and Thickness of Submicron Optical Polymer Films from Transmission Spectra. *Polymers* **2021**, *13*, 2545. [\[CrossRef\]](#)
24. Kumar, R.; Chawla, M.; Rubi, Sharma, A.; Aggarwal, S.; Kumar, P.; Kanjilal, D. Effect of 200 keV argon ion implantation on refractive index of polyethylene terephthalate (PET). *Solid State Phys.* **2012**, *1447*, 607–608. [\[CrossRef\]](#)
25. Shongalova, A.; Correia, M.R.; Teixeira, J.P.; Leitão, J.P.; González, J.C.; Ranjbar, S.; Garud, S.; Vermang, B.; Cunha, J.M.V.; Salomé, P.M.P.; et al. Growth of Sb₂Se₃ thin films by selenization of RF sputtered binary precursors. *Sol. Energy Mater. Sol. Cells* **2018**, *187*, 219–226. [\[CrossRef\]](#)
26. Shongalova, A.; Aitzhanov, M.; Zhantuarov, S.; Urazov, K.; Fernandes, P.; Tokmoldin, N.; Correia, M.R. Comparison of antimony selenide thin films obtained by electrochemical deposition and selenization of a metal precursor. *Mater. Today Proc.* **2020**, *25*, 77–82. [\[CrossRef\]](#)
27. Fernandes, P.A.; Shongalova, A.; Da Cunha, A.F.; Teixeira, J.P.; Leitão, J.P.; Cunha, J.M.V.; Bose, S.; Salomé, P.M.P.; Correia, M.R. Phase selective growth of Cu₁₂Sb₄Si₃ and Cu₃Sb₅S₄ thin films by chalcogenization of simultaneous sputtered metal precursors. *J. Alloys Compd.* **2019**, *797*, 1359–1366. [\[CrossRef\]](#)
28. Moshnikov, V.A.; Gracheva, I.E.; Kuznezov, V.V.; Maximov, A.I.; Karpova, S.S.; Ponomareva, A.A. Hierarchical nanostructured semiconductor porous materials for gas sensors. *J. Non Cryst. Solids* **2010**, *356*, 2020–2025. [\[CrossRef\]](#)
29. Moshnikov, V.A.; Gracheva, I.E.; An'chkov, M.G. Investigation of sol-gel derived nanomaterials with a hierarchical structure. *Glass Phys. Chem.* **2011**, *37*, 485–495. [\[CrossRef\]](#)
30. Shilova, O.A. Synthesis and structure features of composite silicate and hybrid TEOS-derived thin films doped by inorganic and organic additives. *J. Sol Gel Sci. Technol.* **2013**, *68*, 387–410. [\[CrossRef\]](#)
31. Gordillo, G.; Moreno, L.C.; de la Cruz, W.; Teheran, P. Preparation and characterization of SnO₂ thin films deposited by spray pyrolysis from SnCl₂ and SnCl₄ precursors. *Thin Solid Film.* **1991**, *252*, 61–66. [\[CrossRef\]](#)
32. Dmitriyeva, E.A.; Lebedev, I.A.; Bondar, E.A.; Fedosimova, A.I.; Temiraliyev, A.T.; Murzalinov, D.O.; Ibraimova, S.A.; Nurbaev, B.M.; Elemessov, K.; Baitimbetova, B.A. The Influence of Lyophobicity and Lyophilicity of Film-Forming Systems on the Properties of Tin Oxide Films. *Coatings* **2023**, *13*, 1990. [\[CrossRef\]](#)
33. Murzalinov, D.O.; Dmitriyeva, E.A.; Lebedev, I.A.; Bondar, E.A.; Fedosimova, A.I.; Kemelbekova, A.E. The effect of pH solution in the sol-gel process on the structure and properties of thin SnO₂ films. *Processes* **2022**, *10*, 1116. [\[CrossRef\]](#)
34. Dmitriyeva, E.A.; Mukhamedshina, D.M.; Mit', K.A.; Beisenkhanov, N.B. The effect of NH₄F and NH₄OH on the structure and physical properties of thin SnO₂ films synthesized by the sol-gel method. *Glass Phys. Chem.* **2014**, *40*, 31–36. [\[CrossRef\]](#)
35. Volkov, A.I.; Zharsky, I.M. *Large Chemical Handbook*; Modern School: Minsk, Belarus, 2005; 608p. (In Russian)
36. Demartin, F.; Campostrini, I.; Gramaccioli, C.M. Panichiite, natural ammonium hexachlorostannate(IV), (NH₄)₂SnCl₆, from la fossa crater, vulcano, aeolian islands, Italy. *Can. Mineral.* **2009**, *47*, 367–372. [\[CrossRef\]](#)

37. Dincer, C.; Bruch, R.; Costa Rama, E.; Fernández Abedul, M.T.; Merkoçi, A.; Manz, A.; Urban, G.A.; Güder, F. Disposable sensors in diagnostics, food, and environmental monitoring. *Adv. Mater.* **2019**, *31*, 1806739. [[CrossRef](#)] [[PubMed](#)]
38. Yao, S.; Yang, L.; Shi, S.; Zhou, Y.; Long, M.; Zhang, W.; Cai, S.; Huang, C.; Liu, T.; Zou, B.A. Two-in-one annealing enables dopant free block copolymer based organic solar cells with over 16% efficiency. *Chin. J. Chem.* **2022**, *41*, 672–678. [[CrossRef](#)]
39. Faheem, M.B.; Khan, B.; Feng, C.; Farooq, M.U.; Raziq, F.; Xiao, Y.; Li, Y. All-inorganic perovskite solar cells: Energetics, key challenges, and strategies toward commercialization. *ACS Energy Lett.* **2020**, *5*, 290–320. [[CrossRef](#)]
40. Siddhartha; Aarya, S.; Dev, K.; Raghuvanshi, S.K.; Krishna, J.B.M.; Wahab, M.A. Effect of gamma radiation on the structural and optical properties of Polyethyleneterephthalate (PET) polymer. *Radiat. Phys. Chem.* **2012**, *81*, 458–462. [[CrossRef](#)]
41. Kumar, R.; Singh, P. Influence of SHI upon nanohole free volume and micro scale level surface modifications of polyethyleneterephthalate polymer films. *App. Surf. Sci.* **2015**, *337*, 19–26. [[CrossRef](#)]
42. Singh, P.; Kumar, R.; Nambissan, P.M.G. Investigation of in-depth and surface properties of polyethyleneterephthalate thin films after SHI and gamma radiation treatment by means of PALS and AFM studies. *Vacuum* **2015**, *115*, 31–38. [[CrossRef](#)]
43. Mukhamedshina, D.M.; Mit', K.A.; Beisenkhanov, N.B.; Dmitriyeva, E.A.; Valitova, I.V. Influence of plasma treatments on the microstructure and electrophysical properties of SnOx thin films synthesized by magnetron sputtering and sol-gel technique. *J. Mater. Sci. Mater. Electron.* **2008**, *19*, 382–387. [[CrossRef](#)]
44. Avis, C.; Billah, M.M.; Jang, J. Light Effect on Amorphous Tin Oxide Thin-Film Transistors. *Adv. Photonics Res.* **2024**, *5*, 4. [[CrossRef](#)]
45. Ramalingam, K.; Rajaraman, T. Structure-bandgap tunability of metal halide perovskites: Synthesis, spectral, single crystal X-ray structural, BVS, CShM and Hirshfeld surface analysis of piperidinium hexahalostannates(IV). *J. Molec. Struct.* **2023**, *1273*, 134285. [[CrossRef](#)]
46. Subramaniam, M.P.; Arunachalam, G.; Kandasamy, R.; Veluswamy, P.; Hiroya, I. Effect of pH and annealing temperature on the properties of tin oxide nanoparticles prepared by sol–gel method. *J. Mater. Sci. Mater. Electron.* **2018**, *29*, 658–666. [[CrossRef](#)]
47. Mohammed, N.J.; Rasheed, Z.S. Enhancement Optical Characterized of Tin Oxide in Polymer Polyvinyl alcohol Colloid Prepared by Laser Ablation Method. *Baghdad Sci. J.* **2024**, *21*, 2425–2432. [[CrossRef](#)]
48. Lin, C.Q.; Peng, R.X.; Song, W.; Chen, Z.Y.; Feng, T.T.; Sun, D.H.; Bai, Y.Q.; Ge, Z.Y. Multi-component Copolymerized Donors enable Frozen Nano-morphology and Superior Ductility for Efficient Binary Organic Solar Cells. *Angew. Chem. Int. Ed.* **2024**, *63*, 31. [[CrossRef](#)] [[PubMed](#)]
49. Choi, D.H.; Seok, H.J.; Kim, S.K.; Kim, H.K. Highly transparent and conductive Ga-doped InWO multi-component electrodes for Perovskite photovoltaics. *J. Alloys Compd.* **2024**, *1001*, 175018. [[CrossRef](#)]
50. Zeng, G.Y.; Liu, G.Y.; Wang, T.T.; Wen, L.L.; Li, J.N.; Meng, Y.; Li, X. Ionic liquid gel microspheres as multifunctional bi-component additives for the crystallinity manipulation and defect passivation in all-air-processed perovskite solar cells. *Chem. Eng. J.* **2024**, *495*, 153512. [[CrossRef](#)]
51. Hossain, M.I.; Qarony, W.; Ma, S.N.; Zeng, L.H.; Knipp, D.; Tsang, Y.H. Perovskite/Silicon Tandem Solar Cells: From Detailed Balance Limit Calculations to Photon Management. *Nano Micro Lett.* **2019**, *11*, 58. [[CrossRef](#)]

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