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Original Article

Deposited Lead Sulfide Thin Film on Substrate with Chemical Spray Pyrolysis Technique

Ali Qasim Kadhim Jawad[1], Tuqa Salah Ghani Qaddoori[2], Huda Salah Ghani Qaddoori[3]

[1,2,3]University of Technology, Applied Sciences - Laser Science and Technology

Abstract:- Lead sulfide (PbS) thin films have been deposited onto glass and polymide (PI) substrates at 300 0C with chemical spray pyrolysis (CSP) technique. Effects of substrate types on the structural properties of the films were studied. Sets of experiments were conducted to optimize the deposition of PbS films with appropriate deposition parameters. To evaluate the melting point temperature of a PI substrate, thermal studies were performed using a Differential scanning calorimeter. The deposited films were analyzed with X-ray diffraction, energy dispersive X-ray and atomic force microscopy to determine their structural properties. DSC measurement confirmed that the PI material has a glass transition temperature (Tg) of approximately 311°C and has no melting peak. X-ray diffraction patterns reveal that the films exhibit the cubic rock salt (NaCl) type structure. PI substrate exhibited the larger roughness than that for the glass because of large particles adsorbed on the PI substrate.

Keywords : Lead Sulfide, Chemical Spray Pyrolysis, Thin Film on Substrate.

Corresponding Author: Ali Qasim Kadhim Jawad†, University of Technology, Applied Sciences - Laser Science and Technology

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Introduction:

1.1 Lead sulfide (PbS)

PbS is a IV-VI compound semiconductor has a cubic lattice with unit cell face center cube [1]. It is an important direct and narrow gap semiconductor material with band gap energy of 0.4 eV. PbS thin films have be en used in a lot of applications, including electronic and optoelectronic devices. Thin films of PbS have been prepared with various physical and chemical thin film deposition techniques, such as chemical bath deposition (CBD)[2], electrodeposition (ED)[3], chemical spray deposition (CSP) and thermal evaporation technique[4]. Among these different techniques, spray technique is advantageous on account of the low-cost and its suitability for forming large area thin films[5]. Research on PbS on flexible polymeric substrates such as polyimide (PI) is gaining immense interests due to their flexibility, light-weight, low-cost (therefore potentially low-cost devices can be fabricated on top of PI), high temperature resistance (typically up to 400°C processing temperature), low coefficient of thermal expansion (CTE), low moisture uptake and high moisture release characteristics, excellent electrical properties and also increased voltage endurance[6]. Due to its superior properties, PI has found its applications as substrates in flexible thin film solar cells, flexible printed circuits and high density interconnects[7]. In this work, an attempt has been made to study the structural properties of the PbS thin films grown by chemical spray pyrolysis technique on glass and polymide substrates. This paper aims to use of PI plastic as a substrate for thin-film solar cells with chemical spray pyrolysis technique. measurement confirmed that the PI material has a Tg of approximately 311°C and has no melting peak [8].

1.2 chemical spray pyrolysis technique

Chemical spray pyrolysis technique offers a particularly straightforward way to dope films with just about any component in any proportion by simply adding it in some type to the spray resolution. Not like closed vapor deposition ways, spray pyrolysis doesn't need prime quality targets and/or substrates nor will it need vacuum at any stage, that could be a nice advantage if the technique is to be scaled up for industrial applications[9].The deposition rate and also the thickness of the films is simply controlled over a good vary by dynamic these pray parameters, therefore eliminating the main drawbacks of chemical ways like sol ± gel that produces films of restricted thickness. Operative at moderate temperatures (200±600-degree Cent.) SP will turn out films on less strong materials. Not like high-powered strategies like frequency electron tube sputtering (RFMS), it doesn't cause native heating that may be prejudicial for materials to be deposited. There are nearly no restrictions on substrate material, dimension or its surface profile. By dynamic composition of the spray solution throughout the spray method, it is often used to create bedded films and films having composition gradients throughout the thickness. It's believed that reliable elementary kinetic information is additional seemingly to be obtained on significantly well characterized film surfaces, provided the films area unit quiet compact, uniform which no aspect effects from the substrate occur[10]. spray pyrolysis offers such a chance. The spray pyrolysis technique is helpful for the assembly of thin films of easy oxides, mixed oxides, bronze mineral sort oxides, group I-VI, II-VI, III-VI, IV-VI, V-VI, VIII-VI binary chalcogenides, cluster I-III-VI, II-II-VI, II-III-VI, II-VI-VI and V-II-VI ternary chalcogenides, adamantine copper compounds like Cu2ZnSnS4/Se4, Cu2 CdSnS4/Se4, CuGa SnS4/Se4, Cu2InSnS4/Se4, CuIn5S4/Se4 etc[11].

Since the invention of extreme temperature electrical conduction in oxides like Y-Ba- Cu-O, lots of work has been done on their preparation into thin films by SPT. Thin films of those compounds have applications in electronic devices like superconducting quantum interference devices (SQUID) [12]. Some review articles referring to spray shift process and also the range of thin films deposited by SPT for varied applications have appeared within the literature. Pamplin gave a review of clear conductors and a listing in a very conference on spray shift[13]. Viguie and spitz have classified chemical spray deposition method consistent with the sort of reaction. Kern and Tracy have rumored on a high-speed production spray shift method for titanium dioxide antireflection coating for chemical element cells. However, a comprehensive review of all doable thin film materials that would be deposited by SP technique for varied industrial applications has not been undertaken up to now. In this article, the chemical skillfulness of SP technique is incontestable by reviewing the literature on transition metal oxides, metallic mineral kind oxides, binary, ternary and quaternary chalcogenides and superconducting thin films[14].

1.3 Atomization Techinques

The vital operations for the spray pyrolysis technique are (I) preparation of uniform and fine droplets and (II) the controlled thermal decomposition of those droplets in terms of setting, location and time. Typically, commercial nozzle atomizers are used to spray solutions for thin film preparation. However, such nozzle atomizers are neither comfortable to get reproducibly micrometer or submicron size drop nor to manage their size distribution. Consequently, some new or changed spray atomization techniques are developed recently and used effectively for thin film preparations. A number of them are in brief given below.

1-Ultrasonic nebulized atomization

2- Improved spray pyro hydrolysis

3-Corona spray pyrolysis

4-Electrostatic spray pyrolysis

5-Microprocessor based spray pyrolysis[15].

1.4 FABRICATION OF INSTRUMENT

The schematic diagram of a chemical spray pyrolysis system is shows in (Figure1-1). This contains a spray nozzle, a furnace for heating the substrate, and a mechanical system for rotor, thermocouple included temperature controller and air compressor. To measure the flow of solution and air, liquid and air flow meters have been used. The spraying system and furnace are kept inside an airtight metallic chamber of size 60x60x60 cm3 and the outlet of the box is fitted with an exhaust fan to remove the toxic gases produced during the decomposition of the spray solution. The inner surface of the box is painted by epoxy liquid, to reduce the heat loss through the surface [16].

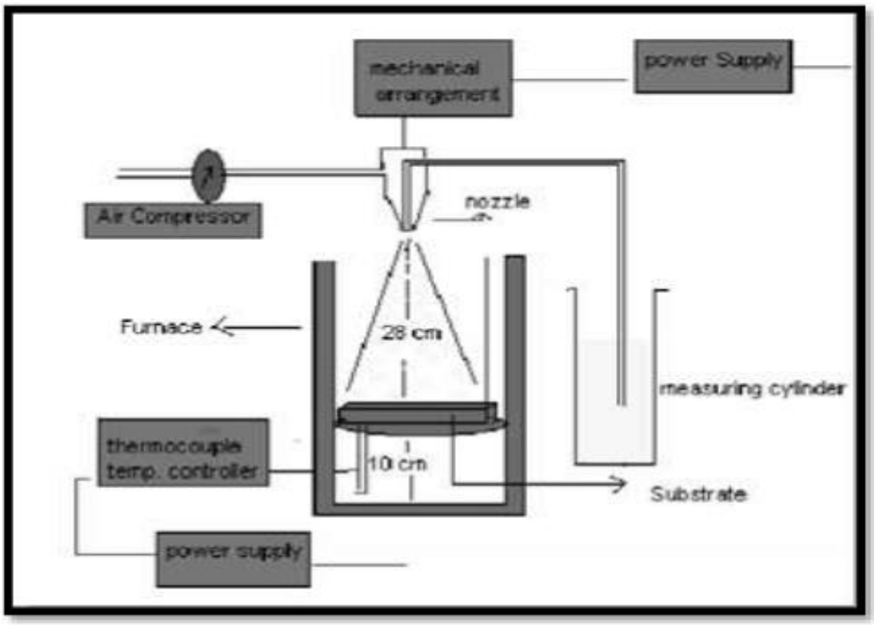

Fig. 1-1. Schematic of Spray Pyrolysis

To maintain the constant temperature of the substrate, a homemade furnace is used. This gives a temperature of up to 6500C for deposition. In order to measure the temperature during the sample preparation, the chrome -alumel thermocouple is used. The nozzle is made of borocil glass, and consists of a solution tube surrounded by a glass bulb. Due to the air pressure of the carrier gas, a vacuum is created at the tip of the nozzle to suck the solution from the tube after which the spray starts. The diameter of the solution tip of the nozzle is nearly 1mm. In the present setup, the substrate is kept stationary, while the nozzle is free for to and fro motion. This can be achieved by using an electrical stepper motor. The substrate to nozzle distance is kept at 25-30 cm. A photograph of the system is shown in Figure (1-2).

Fig. 1-2. Photograph of Spray Pyrolysis

1.5 Kinetics involved in Spray pyrolysis:

The basic principle involved in chemical spray pyrolysis is that when a droplet of the spray solution reaches the hot substrate, owing to the pyrolytic decomposition of the solution, well adherent films are deposited. In this process the solution is pulverized by means of air and arrives on the substrate placed inside the furnace in the form of fine drops known as aerosols which form a thin layer at the substrates. The phenomenon for the preparation of a metal oxide thin film depends on surface hydrolysis of metal chloride on a heated substrate surface in accordance with the equation, [17]

$MCl_x + {}_yH_2O \rightarrow MO_y + {}_xHCl$,

where M is the host metal such as Zn, Cd, In etc. of the oxide films. The spray nozzle with the help of the carrier gases accomplishes the atomization of the chemical solution into aerosols. The temperature of the substrate is maintained at a constant value by using a temperature controlled furnace or hot plate. In general, the films grown at a substrate temperature less than 3000C are amorphous in nature. To get polycrystalline films, one needs to employ higher substrate temperatures or post annealing treatment. The film formation depends upon the droplet lending, reaction and solvent evaporation, which relates to the droplet size. When the droplet approaches the substrate just before the solvent is completely removed, that is the ideal condition for the preparation of the film.

2. Experimental method

2.1 Substrates cleaning

In this experiment, glass and PI plastic were used as substrates. The glass and PI plastic substrate was cleaned by alcohol for 10 min to remove contamination. After the cleaning process, all of the substrates were rinsed with distilled water (DI water).The samples were then dried with nitrogen (N2) gas

2.2 Materials

Lead (II) acetate trihydrate (Pb(CH3CO2)2· 3H2O 99.999%), Thiourea (CS (NH2)2), ≥99.0%) were acquired from Acros Organics.

2.3 Preparation of PbS Solution

A typical PbS solution procedure involves:

1. Thiourea solution [CS (NH2)2]: This solution was prepared with molarities (0.1M), from solving (0.761gm) of

thiourea in (100ml) of distilled water and was marked Solution 1. This solution was vigorously stirred using a magnetic stirrer about 10 minutes.

2. Lead Nitrate solution [Pb(CH3CO2)2 · 3H2O]: This solution was prepared with molarities (0.1M), from solving(2.78gm) of lead acetate in (100ml) of distilled water and was marked Solution 2. This solution was vigorously stirred using a magnetic stirrer about 10 minutes.

3. A Solution 1 was added to Solution 2 and vigorously stirred using a magnetic stirrer and was marked Solution 3.

PbS thin films were deposited form a solution 3 by chemical spray pyrolysis technique on glass and PI substrates. The description of experimental set-up of (CSP) system is presented in (Fig. 2-1). In order to get uniform thin films, the height of the spraying nozzle and the rate of spray process were kept constant during the deposition process at 35 cm and 15 cm3/min. The spraying process lasted about 6 second.The period between spraying processes was about 1 min; this period was enough to avoid excessive cooling of the substrate. PbS thin film was deposited on glass and PI substrates at a temperature of 300 0C and a concentration of 0.1 M. The crystallographic structure of the PbS thin films deposited on the glass and PI substrates was determined with a high resolution X-ray diffractometer system (Model:Panalytical Empyrean) with CuKα radiation (λ) of 0.154 nm.The compositions of the PbS thin films were estimated with energy dispersive X-ray analysis (EDX) (Model JSM—6460LV). The surface morphology of PbS thin films was determined with atomic force microscope (AFM, Model:Ultra Objective).

The thicknesses of the PbS on the glass and PI substrates are of the order of 300 nm, which were measured with an optical reflectometer (Model: FilmetricsF20)

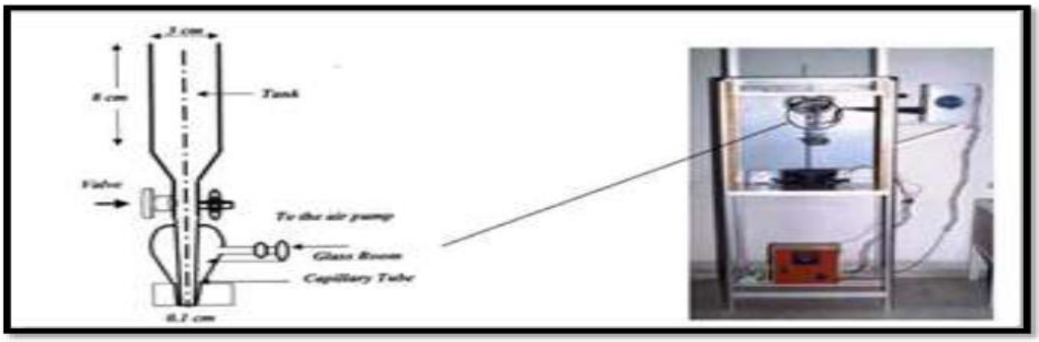

Fig.2-1. Experimental Set-up of Spraying Apparatus (right), and Layout of enlarged spraying glass nozzle (left).

Results and Discussions

3.1 DSC heating curve

The second DSC heating plot curve of the PI substrate heated from 30°C to 500°C in N2 ambient (heating rate =20°C/min) are shown in(fig.3-1). The upwards arrow indicates endothermic reaction. From the figure, glass transition temperature (Tg) of approximately 311.95°C is evident (as shown by the inflection point). This transition is indicated by an increase in heat capacity due to increased molecular motions in the PI substrate[18].

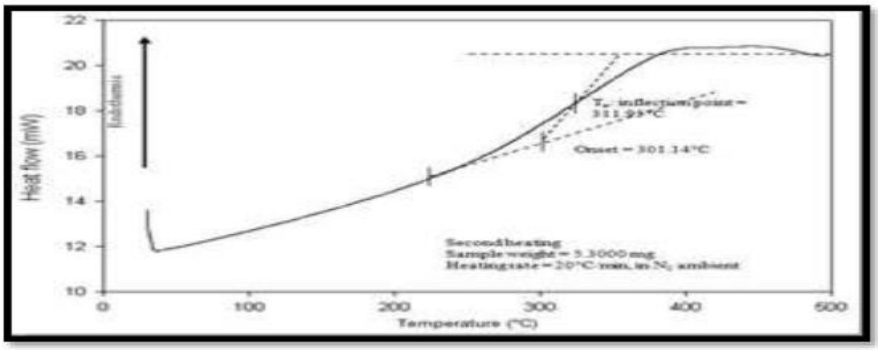

Fig. 3-1 DSC plot of PI substrate.

No melting peak is observed within this temperature range(30 – 500°C) which conforms to the intrinsic property of standard Kapton polyimide 300HN that possesses no melting point.[19].

3.2 The X-ray diffraction patterns of PbS film

The X-ray diffraction patterns of PbS film on PI and glass substrates are shown in Fig. 3-2 PbS film have cubic rock salt(NaCl) type structures. XRD patterns of the PbS thin films showed sharp [1 1 1] and [2 0 0] peaks along with minor peaks of [2 20], [3 1 1] and [2 2 2] planes to cubic structure of PbS thin films, as confirmed by standard ASTM card (No. 030660020).For the PbS thin films on the PET substrate, the main peak, which corresponds to the PI substrate, was observed at the angle 2θ = 22.080 and has a high intensity, as seen in Fig. 3.a.This behavior is in agreement with that reported in the literature[20].

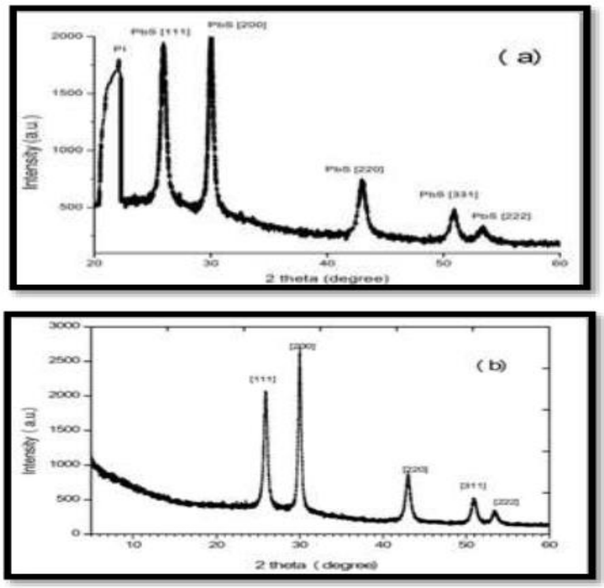

Fig.3-2 XRD patterns of PbS thin film on (a). PI and(b). glass substrate

3.3 EDX analysis for the PbS thin film

The EDX results for the PbS thin film deposited on glass and PI substrate are shown in(Fig.3-3). The EDX analysis confirmed the composition of lead and sulfur in the PbS film. The presence of C and O peaks was due to the PI substrate in (Fig. 4.b).

The presence of Si and O peaks in (Fig. 4.a) is due to the glass substrate

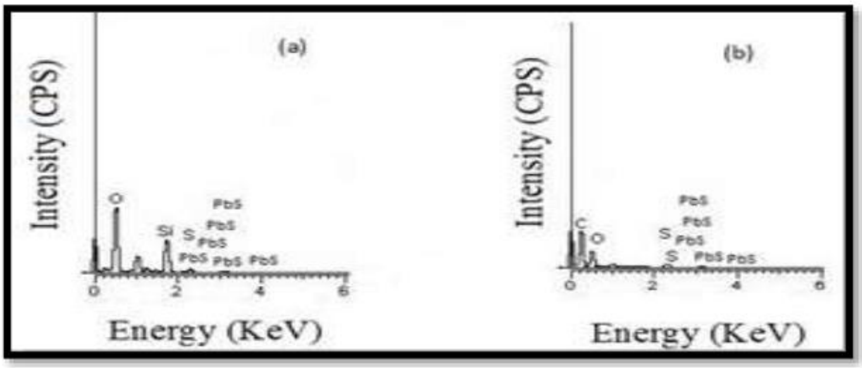

Fig. 3-3 EDX results for PbS thin films deposited on a. glass substrates and b. PI substrates

3.4 AFM analysis of PbS thin films

AFM images of the surface morphologies of PbS thin films on to glass and PI substrates are shown in (Fig. 3-4). The root mean square (RMS) for PI thin films on glass is 9.62 nm, and that the RMS for PI substrates is 12.62 nm. The increase of roughness is due to the large particles that are absorbed on the PI substrates. Obviously, the PbS films on glass have smoother surfaces than those on PI substrates.

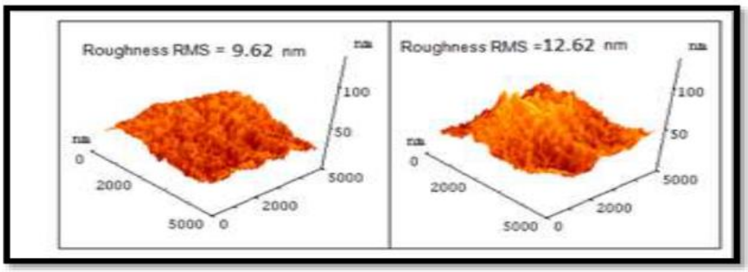

Fig. 3-4 AFM analysis of PbS thin films deposited on a. glass substrate, b. PI substrate.

4-1 Conclusions

Lead sulfide thin films were deposited onto polymide and glass substrates at 300 ^{0}C with chemical spray pyrolysis technique. The PbS thin films were found to have different roughness values when deposited on glass and compared to when they are deposited on PI substrates. X-ray diffraction patterns confirm the proper phase formation of the PbS. DSC measurement confirmed that the PI material has a Tg of approximately 311°C and has no melting peak

4-2 References

1. D. Kumar, G. Agarwal, B. Tripathi, D. Vyas, and V. Kulshrestha, “Characterization of PbS nanoparticles synthesized by chemical bath deposition,” J. Alloys Compd., vol. 484, no. 1–2, pp. 463–466, 2009.
2. L. Raniero, C. L. Ferreira, L. R. Cruz, A. L. Pinto, and R. M. P. Alves, “Photoconductivity activation in PbS thin films grown at room temperature by chemical bath deposition,” Phys. B Condens. Matter, vol. 405, no. 5, pp. 1283– 1286, 2010.
3. M. Sharon, K. S. Ramaiah, M. Kumar, M. Neumann-Spallart, and C. Levy- lement, “Electrodeposition of lead sulphide in acidic medium,” J. Electroanal. Chem., vol. 436, no. 1–2, pp. 49–52, 1997.
4. S. Kumar and R. Chandra, “INFLUENCE OF LASER FLUX DENSITY ON THE SURFACE MORPHOLOGY OF LEAD SULPHIDE THIN FILMS.,” Chalcogenide Lett., vol. 6, no. 6, 2009.
5. H. H. Afifi, S. A. Mahmoud, and A. Ashour, “Structural study of ZnS thin films prepared by spray pyrolysis,” Thin Solid Films, vol. 263, no. 2, pp. 248–251, 1995.
6. F. Kessler and D. Rudmann, “Technological aspects of flexible CIGS solar cells and modules,” Sol. Energy, vol. 77, no. 6, pp. 685–695, 2004.
7. A. N. Tiwari, A. Romeo, D. Baetzner, and H. Zogg, “Flexible CdTe solar cells on polymer films,” Prog. Photovoltaics Res. Appl., vol. 9, no. 3, pp. 211–215, 2001.
8. M. G. Faraj and M. Z. Pakhuruddin, “Deposited lead sulfide thin films on different substrates with chemical spray pyrolysis technique,” Int. J. Thin Film. Sci. Technol., vol. 4, no. 3, p. 215, 2015.
9. T. Sall, M. Mollar, and B. Mar'\i, “Substrate influences on the properties of SnS thin films deposited by chemical spray pyrolysis technique for photovoltaic applications,” J. Mater. Sci., vol. 51, no. 16, pp. 7607–7613, 2016.
10. D. Perednis and L. J. Gauckler, “Thin film deposition using spray pyrolysis,” J. electroceramics, vol. 14, no. 2, pp. 103–111, 2005.

11. S. M. Sabnis, P. A. Bhadane, and P. G. Kulkarni, “Process flow of spray pyrolysis technique,” J. Appl. Phys., vol. 4, no. 5, pp. 7–11, 2013.

12. P. S. Patil, “Versatility of chemical spray pyrolysis technique,” Mater. Chem. Phys., vol. 59, no. 3, pp. 185–198, 1999.

13. A. Gupta, D. K. Pandya, and S. C. Kashyap, “Thin fluorine-doped tin oxide films prepared using an electric field-modified spray pyrolysis deposition technique,” Jpn. J. Appl. Phys., vol. 43, no. 12B, p. L1592, 2004.

14. K. O. Ukoba, A. C. Eloka-Eboka, and F. L. Inambao, “Review of nanostructured NiO thin film deposition using the spray pyrolysis technique,” Renew. Sustain. Energy Rev., vol. 82, pp. 2900–2915, 2018.

15. M. Marin, F. Poteca\csu, O. Poteca\csu, and F. B. Marin, “Image Analysis Software for Porosity Measurements in Some Powder Metallurgy Alloys,” in Advanced Materials Research, 2017, vol. 1143, pp. 103–107.

16. B. Godbole, N. Badera, S. B. Shrivastav, and V. Ganesan, “A simple chemical spray pyrolysis apparatus for thin film preparation,” Jl. Instrum. Soc. India, vol. 39, no. 1, pp. 42–45, 2009.

17. H. Hartnagel, Semiconducting transparent thin films. CRC Press, 1995.

18. H. Gleskova and S. Wagner, “Amorphous silicon thin-film transistors on compliant polyimide foil substrates,” IEEE Electron Device Lett., vol. 20, no. 9, pp. 473–475, 1999.

19. C. Guillen and J. Herrero, “Electrical contacts on polyimide substrates for flexible thin film photovoltaic devices,” Thin Solid Films, vol. 431, pp. 403–406, 2003.

20. M. Z. Pakhuruddin, K. Ibrahim, A. A. Aziz, and others, “Thermally evaporated thin film microcrystalline silicon solar cells on polyimide substrate with multiple light trapping schemes,” Optoelectron. Adv. Mater. Commun., vol. 8, no. 3–4, pp. 255–259, 2014.