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# DEVELOPMENT OF SPRAY PYROLYSIS SYSTEM FOR DEPOSITION OF NANO-STRUCTURE MATERIALS

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**Abstract.** *In this paper, we report the development of the spray pyrolysis technique for preparing different nano-structure materials toward the application in thin film solar cells. The spray pyrolysis system can heat up the substrate to 600˚C with less than 0.01% full scale. The ramping rate can be set to 10˚C per minute. The effective coating area can be up to $100 \times 100$ mm$^2$. Using this technique, the thickness and roughness of the films can be controlled. The obtained morphology, the microstructure of the thin-films, given by scanning electron microscope, X ray diffraction showed that the system is suitable for deposition of different layers of the dye sensitized solar cell.*

*Keywords: spray pyrolysis system, dye sensitized solar cell, $TiO_2$, CZTS.*

## I. INTRODUCTION

Spray pyrolysis is a physic-chemical technique for deposition of a membrane on a surface, especially for recent development of the dye sensitized solar cell [1–4]. This technique is normally processed first of all by driving different precursors using an inert gas ($N_2$, Ar...) through a nozzle from which the precursors can be well mixed followed by the chemical reactions on the heated surface. Unlike many other techniques, spray pyrolysis represents a very simple and relatively cost-effective one, especially regarding equipment cost. Spray pyrolysis system includes an atomizer, a precursor solution container, a substrate heater and a temperature controller. In this work, it aims at depositing various materials towards the application in thin film solar cell. In order to obtain a high quality membrane, one must pay attention to the following parameters when design and develop the system: the solution flow rate, the substrate temperature and the nozzle characteristics. The aerosol flow rate ($F_a$) is influenced by the liquid properties; the vapor pressure

$(P)$, the viscosity $(\eta)$ and the surface tension $(\sigma)$ as formulated in Eq. (1):

$$F_a = K\sqrt{\frac{P}{\eta . \sigma}} \quad (1)$$

where $K$ is a coefficient depending on the necessary power to generate the aerosol. From the Eq. (1), any addition of an additive to the precursors solutions can change the viscosity, the surface tension, thus change the aerosol flow rate.

In spraying technique, the nozzle capacity varies with the spraying pressure and generally related as in Eq. (2).

$$\frac{Q_1}{Q_2} = \frac{(P_1)^n}{(P_2)^n} \quad (2)$$

where $Q_1$ is the known capacity at pressure $P_1$, and $Q_2$ is the capacity to be determined at pressure $P_2$. In general, the nozzle characteristics as inner diameter, nozzle type like hollow cone, full cone, flat spray, solid stream or spiral type and the nozzle material are already defined by the manufacturer. The substrate temperature must also be controlled because it involves solvent evaporation and precursor decomposition processes and it is the key parameter determining the film morphology and properties. The spray pyrolysis system, in this work, needs meet the following requirements 01) controllable flow rate; 02) controllable substrate temperature (from room temperature to 600°C) with high accuracy; and 03) changeable spraying ambient. The system should be applicable with different materials; easy to change the nozzle and easy to be upgraded.

The system was expected to be applicable for deposition of materials aiming at the use in DSSC and CZTS solar cell.

## II. EXPERIMENTAL

### Building the spray pyrolysis system

The schematic of the spray pyrolysis system is illustrated in Fig. 1.

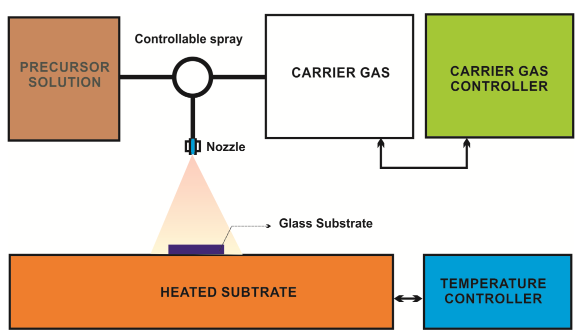


**Fig. 1.** Schematic of spray pyrolysis system.

The precursor solution and carrier gas flow rate were controlled by using the mass flow controller with the built-in and customized software, MS series from Alicat Scientific.

The coverage of spray patterns as calculated from the included spray angle of the spray and the distance from the nozzle orifice (Do). In this work, the desired spray coverage was 450, then the distance was set around 160 mm. The distance should be adjusted accordingly to the final coverage and the substrate area.

**Table 1.** specific parameters of the nozzle

| | |
|---|---|
| Orifice inner diameter (mm) | 0.2 |
| Max gas consumption (L/min) | 11 |
| Max spray pressure (MPa) | 0.1-0.19 |
| Max flow rate of solution (ml/min) | 12 |

The heated substrate is made of bulk aluminum whose the dimensions are $200 \times 200 \times 20$ mm$^3$. The nozzle is made of stainless steel (the nozzle material can be changed), full cone spray type utilizing an internal vane to provide a uniform, round, full spray pattern with medium-to-large sized drops. Temperature was controlled by PID temperature controller with solid state relay TC4S from Autonics.

**Deposition of nano-structure materials**

***Deposition of $TiO_2$ layer***

In dye sensitized solar cell, the $TiO_2$ nanoparticles act as a roadway for the electrons created by the light exciting from the dye sensitized complex. In this work, the $TiO_2$ solution was prepared by sol-gel technique, adapted from [5,6]. The precursors for $TiO_2$ sol-gel were Tetrapropylorthotitanat ($C_{12}H_{28}O_4Ti$) and acetylaceton ($C_5HO_2$ were purchased from Merck, Germany. Isopropyl alcohol (C3H7OH), ethanol (C2H5OH) and nitric acid 65% ($HNO_3$) are from China.
First of all, the glass substrate was cleaned by sonicating using distilled water and ethanol followed by rinsing in water and air-dried. The substrate was heated at 150 0C in open atmosphere. The nozzle was fixed 15 cm from the surface and the carrier gas pressured was 0.5 MPa. After spraying, the samples were heated up 400oC then annealed in air for 30 minutes. The temperature ramping is adjustable [7].

***Deposition CZTS layer***

Thin film of $Cu_2ZnSnS_4$ (CZTS) have attracted significant interest as alternative absorber layers in Cu(In,Ga)(S,Se)$_2$ (CIGS) thin film solar cell. This type of absorber derives from the $CuInSe_2$ chalcopyrite structure by substituting half of the indium atoms with Zinc and the other half with Tin. In this work, the precursor for CZTS layer composed of $CuCl_2.2H_2O$ (crystal 99.6%), SnCl4.5$H_2O$ (crystal 99.6%), $ZnCl_2$ (crystal 99.6%), CS $(NH_2)_2$ (crystal 99.5%); $C_2H_5OH$ (solvent 99.7%) and DI water. The precursors including chloride salts and thiouera, well solved in de-ionized water, were mixed together and stirred for 15 minutes to form homogeneous solution. After that the solution was sprayed on heated substrate at proper distance from spray head to substrate, volume of the spray solution was 40ml, and the spray rate was 1 ml/min [8].

The morphology of the obtained films were studied using a Scanning Electron Microscope (FESEM, S4800-Hitachi) meanwhile the XRD measurements (Bruker D8 Advance Diffractometer); and the surface profilers were used to monitor the thickness of the membranes.

## III. RESULTS AND DISCUSSION

### TST1303 system characteristics

The spray pyrolysis system is named in TST1303 was first built and depicted in Fig. 2. The performance of the system was evaluated empirically by adjusting the parameters like temperature, flow rate, pressure and the spraying height. The evaluation results (not listed in here) showed that TST1303 can heat up the substrate to 600˚C with ±0.01˚C accuracy full scale. The actual temperature can also be measured by external thermometer. The ramping rate can be set up to 10˚C per minute. The effective coating area, in this work, can be up to $100 \times 100$ mm$^2$ and can be expandable in case necessary. The system was tested with $TiO_2$, a roadway for the electrons created by the light exciting from the dye sensitized complex; and CZTS, an alternative absorber layers in CIGS thin film solar cell.

**Fig. 2.** The actual spray pyrolysis system TST1303

### *X-ray diffractogram*

The X-ray diffractograms of the lms, annealed at different temperature, are depicted in Fig. 3. In case of $TiO_2$ deposition, Fig. 3(a), all the X-ray vibration peaks, plotted using raw data, of the synthesized material are well matched with the standards tags of $TiO_2$ in anatase (when substrate temperature was at 500˚C) and rutile phase. The average diameter of the anatase $TiO_2$ was about 20 nm.

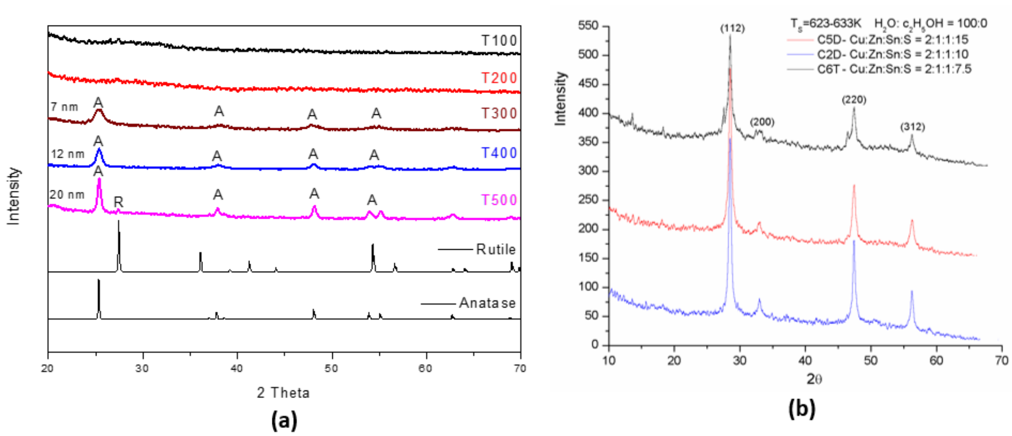


**Fig. 3.** The X-ray diffractograms of obtained nano structure $TiO_2$ and CZTS

The structural characterization of CZTS samples is determined by XRD and depicted in Fig. 3(b). From the X-ray spectra, for all sample, the peaks corresponding to the (1 1 2), (2 0 0), (2 2 0), (3 1 2) planes are characteristic of the kesterite structure of CZTS. The crystalline grain size of the films deposited with different thiourea concentration was calculated to be approximately 28 nm.

### SEM Micrograhps of thin film

The scanning electronic microscope imaging illustrated in figure indicates a porous structure in the nanocrystalline $TiO_2$ and CZTS thin film.

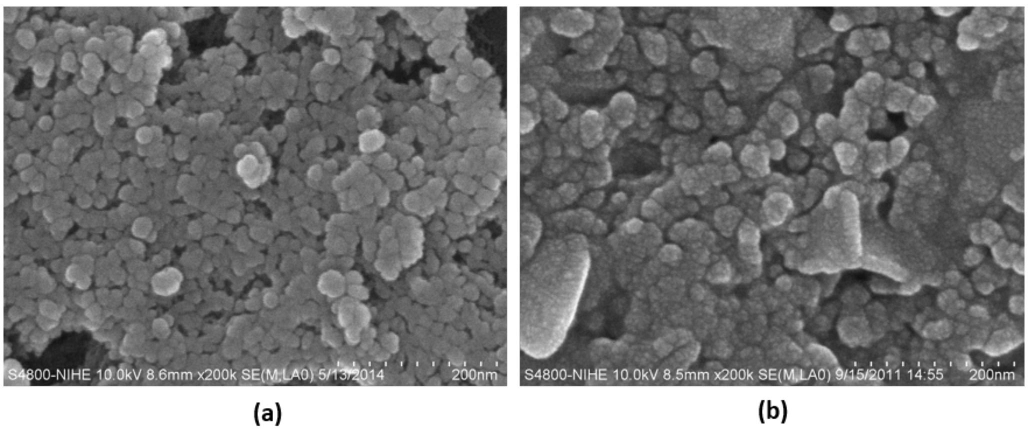


**Fig. 4.** SEM image of nanoporous $TiO_2$ film (a) and Pt film (b).

The system is capable of creating the homogenous membrane; the nanoparticles were well distributed which supposed to facilitate the binding with the dye complex, in case of DSSC; and the N-type semiconductor in case of CZTS solar cell. Thickness verification The thickness of $TiO_2$ was evaluated by Alpha Step IQ at Vietnam Academy of Science and Technology.

The thickness and the roughness of membrane can be changed by adjusting the spraying time (cycles), the spraying height as well as the substrate temperature. The system can also be applicable for depositing a very thin layer of material by changing the nozzle orifice, programmable MFC and the ambient in

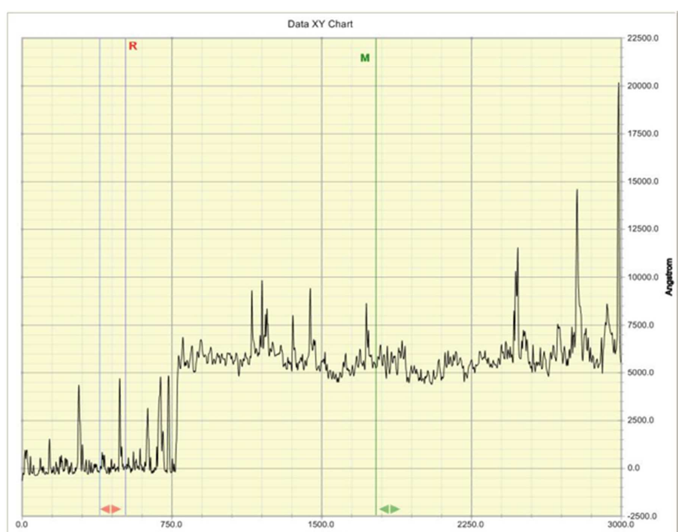


**Fig. 5.** The thickness of $TiO_2$ film given by Alpha Step IQ.

the chamber. Weve also studied other properties of the nano materials like transparent and absorption spectroscopy; Raman spectroscopy; approximated band gap. The obtained results (not discussed in this paper) showed that the system is capable of depositing different nano structure materials that can be used for solar cell development.

## IV. CONCLUSION

In this paper, the development of the spray pyrolysis system, aiming at the deposition of nano structure materials in solar cell, was reported.

The operating parameters of the system including substrate temperature, flow rate, pressure, spraying height, carrier gas, are manual and easy to adjust to meet the empirical requirement. Different precursor like $TiO_2$, CZTS and H2PtCl6 in ethanol (not discussed in this paper) have been sprayed to deposit the nano structure layer in solar cell. The $TiO_2$ film was formed in anatase phase at 500oC using $TiO_2$ solution ($H_2O$ as solvent) meanwhile with $CuCl_2.2H_2O$, $ZnCl_2$, $SnCl4.5H_2O$, CS(NH2)2 precursor solution in $H_2O$ solvent, the Kesterite phase of CZTS was obtained at 360oC substrate temperature. The analysis showed that by adjusting the operating parameters of the system, its possible to optimize properties of the nano structure membrane. Further R&D are being dedicated to improve the automation level of the system according to which the system will be PC interfaced or operated by embedded Windows OS device. The precursor amount can be brought in to the reaction surface by applying the pulse flow rate and the spraying height could be adjusted accordingly to the target material and the spraying area.

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