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Development of an Automated Nebulizer Spray Pyrolysis System and Its Application in the P-N junction Diode Fabrication

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Abstract: An automated nebulizer spray pyrolysis (ANSP) system is developed for fabricating p-Zn:CuO/n-Si junction diode. The mechanical carriage for the X-Y movement and the proposed ANSP system is designed using the SolidWorks design software tool. ATmega-328 microcontroller-based control system was developed to control and move the spray nozzle in the X and Y-axis direction. Zn:CuO (p-type) precursor solution is sprayed on the silicon wafer (n-type) using this ANSP system to form p-Zn:CuO/n-Si junction diode. The process parameters and operating conditions were optimized. The fabricated p-Zn:CuO/n-Si junction diode parameters such as ideality factor (η) and barrier height (φb) were studied under dark and light conditions using Keithley electrometer. The investigation results revealed that the junction diode has the lowest ideality factor and barrier height.

Keywords: Nebulizer; spray pyrolysis; microcontroller; diode; ideality factor; barrier height.

1. INTRODUCTION

Chemical spray pyrolysis (CSP) is easily adaptable deposition technique for the preparation of single and multi-layered thin or thick films. Various type of chemical spray pyrolysis technique has been studied to find out the reliable and cheapest method of preparing thin films. On the other hand, the type of atomizer used in the system can also determine the classification of the spray pyrolysis. An ordinary CSP system comprises of a stationary atomizer, air compressor, temperature controller, and solution chamber. The atomization technique of the CSP system involves spraying a precursor solution on the heated substrate with the help of compressed air through a suitable spray nozzle. The atomizer converted the precursor solution into the mist form of an aerosol. Actually, the size of the aerosol is depends on the type of the atomizers, which determines the film quality. The CSP system used four types of atomizers: air pressurized (the pressurized air tends to produce the fine droplets), electrostatic (the electrostatic force tends to produce the fine droplets), ultrasonic (high ultrasonic frequency tends to produce the fine droplets) and air nebulizer [1-3]. In comparison with these atomizers, air/jet nebulizer atomizer has many advantages including low cost, easy to access and adjustment during the deposition. It can easily produce a droplet size of 0.1-2 µm and the minimum atomization rate is 0.5 cm³/min [4]. Recently, various research articles regarding nebulizer-based spray pyrolysis system have been published. Balaji et al. reported on the preparation of Ru doped MoO₃ thin films and n-RuMoO₃/p-Si junction diodes by jet nebulizer spray pyrolysis system [5]. Sumathi et al. presented the tungsten disulfide (WS₂) thin film deposition process using jet nebulizer spray pyrolysis (JNSP) technique [6]. We also demonstrated the preparation of CuO thin films using the JNSP system [7].
Generally, the quality of the film prepared by the nebulizer spray pyrolysis system relies on the different parameters such as temperature, precursor solution, spraying rate, and spray nozzle movement. Among these, spray nozzle movement considered an important parameter that determines the quality of the film strongly. However, the variation in the nozzle movement leads to uneven spraying on the substrate. Hence, thin film deposition was carried out by keeping the spray nozzle at stationary position in the manual nebulizer spray pyrolysis system. Only a few research reports are available on the determination of the thin film quality by modifying the spray nozzle movement. In recent years, the microcontroller-based automation system is applied to move the spray nozzle for improving the film quality. The simplified lowcost microcontroller based automated spray pyrolysis was developed by Sangle et al. The author strongly recommended that advanced microcontroller based spray pyrolysis technique can improve the quality of coating significantly[8]. Senthilnathan et al. fabricated a low-cost microcontroller spray pyrolysis system to automate the intermittent spray process that produces good quality thin films [9]. Gottliebe at al. utilized mechanical arrangement to move the spray nozzle in x-y direction above the substrate which resulted in the formation of film with uniform thickness over a large surface area [10].

The main aim of our work is to develop a novel and low-cost automated nebulizer spray pyrolysis (ANSP) system and fabricating p-Zn:CuO/n-Si junction diode by using it. Importantly, the diode parameters such as ideality factor and barrier height were calculated and interpreted based on the influence of automated spray nozzle movement in the device performance. This ANSP system has x-y movement for the spray nozzle to facilitate large area (200 x 200 mm) deposition. The novelty of our automated nebulizer spray pyrolysis system (ANSP) system confide on changing the spraying method in the existing manual nebulizer spray pyrolysis system in which the deposition process completely depends on the automated spraying process. Developing and demonstrating the ANSP system we are the first to report on the diode properties of p-Zn:CuO/n-Si junction diode.

2. EXPERIMENTAL DETAILS

2.1 Experimental encounters on the existing nebulizer spray pyrolysis system

The experience and analytical knowledge about the present manual nebulizer spray pyrolysis system played a vital role in designing and developing a novel ANSP system. More importantly, the accumulated knowledge helps to find out the practical problems experienced with the previous system and to shape the instruments to overcome those practical problems. Gowthami et al. prepared NiO thin films using a simple nebulizer spray pyrolysis system. [11] The system is shown in Figure 1 (a). The deposition process was done by spraying on the glass substrate through the ‘L’ type of glass tube in which the glass tube was narrower towards the substrate side. In this system, the ‘L’ type of glass tube was employed as a spray nozzle which was held in a stationary position. There was a problem that existed with regard to SEM images of NiO films. It exhibits irregular shape grains and agglomerated structures which may occur due to inappropriate spraying process [11]. Another experimental setup of the nebulized spray pyrolysis technique reported by Raj Mohamed et at. is shown in Figure1(b) [12]. This instrument also has the same type of glass tube as mentioned in the previous system and it acts as a spray nozzle where sprayed in a stationary position. Recently, Deepa and Nagaraju jampan designed and developed an automated ultrasonic spray pyrolysis system [13]. Fig 1 (c) exhibits the schematic setup of the system. Instead of jet nebulizer, the author used ultrasonic nebulizer as a spray nozzle and it is attached in the spray head. The beauty of this system is the spray head can able to move in x-y direction using the digital spray model created by ‘slice3r’ software to facilitate large area deposition. The author reported that the automation system helps to obtain good quality CZTS thin films. Though it was a good system, the use of ultrasonic nebulizer and sophisticated software makes the system cost high.
2.2 Design model of ANSP system

SolidWorks is one of the magnificent parametric 3D modeling design tool. It helps the designers to draw their ideas, define the dimensions, and create 3D models with detailed drawings [14-15]. Generally, it is advisable to start with a basic sketch on papers before working on the SolidWorks design tool. The designer should follow a few steps for designing their desired model. At first, the dimensions of each part should be decided to create a suitable design. In the second step, all the parts should model individually. Finally, draw and check the appropriate model for additional improvements. Figure 2 (a) illustrates mechanical carriage design for the X-Y movement and Figure 2 (b) shows the final 3D model of the proposed ANSP system. Both 3D models were designed using SolidWorks. As observed in figure 2 (a) and (b), the mechanical carriage for the X-axis movement is designed to hold a nebulizer attached with a spray nozzle. Another mechanical carriage is designed to hold X-axis mechanical carriage and to move them in Y-axis direction.

Figure 2. (a) Mechanical carriage design for the X-Y movement (b) Final 3D design model of the proposed ANSP system
2.3 Selection of hardware components
The choice of microcontroller is an important work to fulfill the designer task and system requirement. While choosing the microcontroller, we should consider a few criteria such as speed, power consumption, cost, peripherals, memory, and availability. In recent years, Arduino ATmega-328 microcontroller has been used for various applications due to their advantages of low cost, easy availability and user friendly. In our system, we have used AVR based low power CMOS ATmega328 8-bit microcontroller to control the X-Y movement of the spray nozzle. This microcontroller acts as a processor for the Arduino Uno board. It consists of 28 I/O pins, ADC, serial programmable UART, and timer/counters. Basically, the Arduino ATmega-328 microcontroller is programmed to drive the motor drive for control the motors. Recently, Harisudhan et al. reported on rotating stepper motor by using Arduino microcontroller and strongly suggested that Arduino programmed stepper motors can be mainly applicable for the automation process [16]. Figure 3(a) shows ATmega 328 microcontroller-based Arduino Uno development board which was used in the ANSP system. Driving the motor was considered as a critical task in our work. Therefore a suitable motor driver is required for a smooth motor driving. H-bridge configuration based L293N motor drivers were used to drive two stepper motors for the X-Y movement which is shown in Figure 3(b). The advantage of using this motor drive is the speed of the stepper motor can be varied with respect to the width of pulses in PWM. Two separate switch mode power supply (SMPS) are used to supply 2Amps current for operating L293N motor driver. It can offer a higher current output in a low voltage and also it ensures the smooth operation for the system. Figure 3(c) shows 2A-SMPS module. There are two stepper motors are required to move the spray nozzle in the X and Y-axis direction. The selection of stepper motor should be based on the step angle, steps per revolution, operating current, and holding torque. Figure 3(d) shows the stepper motor used in our ANSP system.

Figure 3. (a) Arduino Uno-ATmeg328 development board (b) L293N motor driver board (c) 2A SMPS module (d) Stepper motor

2.4 Construction of control system
ANSP system is designed and developed to make the thin film deposition process easier with a controlled manner. Figure 4 shows the hardware construction of the control system unit for the ANSP system which incorporated all of the above components.
Figure 4. Hardware construction diagram of the control system

It consists of ATmega328 microcontroller, L293N drivers, SMPS, stepper motors, push button switches and LCD module. Two stepper motors were used to move the spray nozzle in the X and Y direction. X-axis mechanical carriage was driven by one stepper motor through rack and pinion method. Similarly, Y-axis mechanical carriage was driven by another stepper motor through the same rack and pinion method. ATmega328 microcontroller can operate at low voltages and it requires a small amount of current to operate. But the stepper motors are required a high voltage and current to rotate. Generally, microcontrollers are designed only to supply milliamps (mA) of current from its I/O pins. This current will not be sufficient to drive the stepper motors. Therefore L293N H-bridge motor driver is employed to provide sufficient current and control both speed and rotating direction of the stepper motor. There are two voltage pins in the L293N driver, one pin is used to get the current for working and another pin is used to supply the required current for the stepper motors. Figure 5 (a-b) shows an actual photograph of the control system with its power supply unit for the ANSP system.

Figure 5. Photographic images of control system unit (a) front view (b) inside view (c) SMPS unit

2.5 Software implementation
Arduino Integrated Development Environment (IDE) is a programming environment that allows the user to program. This open source software is mainly used for writing, compiling and loading the code
into different Arduino devices. It can work on high level programming language like c and c++. The program to be executed for the spray nozzle movement can be done by using the Arduino IDE. According to the deposition process, the program can be edit and modify at any time. These programs are uploaded in the ATmega328 microcontroller by using power jack USB cable. The executed programs are stored in the internal memory storage (ROM) of the microcontroller. Arduino Uno development board has a reset button. The purpose of this reset is to reset the uploaded program based on the requirement. While uploading the program, the control system unit should be connected with stepper motors of the X-Y mechanical carriage. Once the programs are uploaded to the microcontroller, the ANSP system is ready to operate.

2.6 Working of the ANSP system

In its final form of the ANSP system shown in Figure 6, the control system incorporated with the mechanical carriage to operate the spray nozzle in the X-Y axis direction. Initially, a substrate heater is set to constant temperature by the temperature controller. The substrate to be sprayed should be kept on the heater. Many trials were conducted to optimize the air pressure by increasing the pressure form 1 to 5 kg/cm². At last, we found 2.1 kg/cm² is the best optimized constant air pressure for smooth deposition. The spray nozzle is moved and placed accurately on top of the substrate with the help of four push button switches. All the deposition parameters should be set before starting the deposition process. According to the preloaded program in the microcontroller, it sends the signals to the driver units for spinning the stepper motor in the X and Y-axis movement. The precursor solution is filled at the bottom portion of the nebulizer. When the air compressor is being switched on, the flow of air passed to the nebulizer with high pressure. As a result, the flow of air changed the solution into aerosol and passed through the spray nozzle. The aerosol is sprayed on the heated substrate.

![Figure 6. ANSP system in its final form](image-url)
2.7 Fabrication of p-Zn:CuO/n-Si junction diode

A schematic arrangement of p-Zn:CuO/n-Si junction diode fabricated by the ANSP system as shown in Figure 7. Zn doped CuO precursor solution is sprayed on the silicon wafer to form the P-N junction diode. The influence of Zn incorporated into CuO was clearly explained in the earlier research reports [17-18]. To synthesis p-type Zn:CuO precursor solution, precursor material copper (II) nitrate and doping material zinc nitrate were mixed in 10 ml of distilled water. The mixed solutions were stirred for 1 hour using a magnetic stirrer to obtain a final spraying precursor solution. The optimized parameters of the precursor solution and deposition conditions are illustrated in table 1. 279µm thickness of one side polished n-type silicon wafer was used as an n-type substrate. The wafer cleaning process is a critical task in diode fabrication. The wafer with unwanted impurities may affect diode properties which lead to very poor device performance [19-20]. RCA cleaning is a universally accepted cleaning procedure developed by Werner Kern for cleaning the silicon surface. The RCA cleaning procedure comprises a two-step procedure: standard clean 1 (SC1) and standard clean 2 (SC2). The detailed RCA procedure involves the following steps.

i) All the silicon wafers are rinsed in acetone and IPA (isopropyl alcohol) solution for removing dirt from the wafers.

ii) To remove native oxide, wafers are dipped for about 30 sec in 2% HF solution

iii) The wafers are immersed in NH₄OH:H₂O₂:H₂O(1:2:7) and heated to (70-80)°C for 10 minutes to remove the organic contaminates. This is known as SC1 step.

iv) Again, wafers are rinsed in HF solution to remove native oxide formed after SC1

v) Finally, the SC2 step is used to remove heavy alkali ions and cations on the wafer which is immersed in HCl:H₂O₂:H₂O (1:2:7) solution and heated at 75-80°C for 10 minutes.

The prepared Zn:CuO precursor solution of 5ml was deposited on the RCA cleaned n-Si wafer by the ANSP system at a constant temperature of 450°C. At first, the well-cleaned wafer was kept on the hot plate of the substrate heater. A specially designed spray nozzle with 0.1mm diameter is attached to the nebulizer. This arrangement was fixed at the top of the X-axis mechanical carriage and the precursor solution was filled at the bottom portion of the nebulizer. The distance between the spray nozzle and the wafer was fixed at 5 cm manually. The spray nozzle was correctly positioned on the top of the wafer using the left, right, and up, down push button in the control unit. After setting all the necessary parameters, the air has impinged into the solution. As a result, the flow of air sprays the aerosol on the wafer substrate. According to program, the spray nozzle moves in X and Y-axis direction till the solution was finished in the nebulizer. After the deposition, silver (Ag) paste was applied on the both side of the p-Zn:CuO/p-Si junction diode for establishing ohmic contact.

Figure 7. Schematic diagram of p-Zn:CuO/n-Si junction diode structure
Table 1. Optimized deposition parameters and operating conditions

<table>
<thead>
<tr>
<th>Process parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole concentration (M)</td>
<td>0.3</td>
</tr>
<tr>
<td>Zn doping (wt %)</td>
<td>3</td>
</tr>
<tr>
<td>Substrate temperature (°C)</td>
<td>450</td>
</tr>
<tr>
<td>Nozzle to wafer distance (cm)</td>
<td>5</td>
</tr>
<tr>
<td>Air pressure (kg/cm²)</td>
<td>2.1</td>
</tr>
<tr>
<td>Spraying volume (ml)</td>
<td>5</td>
</tr>
<tr>
<td>Deposition time (min)</td>
<td>3</td>
</tr>
</tbody>
</table>

3. RESULT AND DISCUSSION

3.1 Investigation of the p-Zn: CuO/n-Si junction diode

I-V characterization arrangement of p-Zn:CuO/n-Si junction diode using high resistance keithley 6517B electrometer shown in Figure 8.

Figure 8. Schematic diagram of p-Zn:CuO/n-Si junction diode

The p-Zn:CuO/n-Si junction diode was fabricated by the ANSP system based on the optimized and process parameter results. The forward and reverse bias conditions were measured by applying constant bias voltage from -4 to +4 using Keithley source meter. According to the electrical investigation of bias voltage versus current, we measured the junction diode parameters such as ideality factor ($\eta$) and barrier height ($\phi_b$) under darkness and illumination of light (Tungsten halogen and metal halide – 100 mW/cm²) conditions [21-22]. Figure 9 (a) shows the I-V characteristics of p-Zn:CuO/n-Si junction diode. As observed in Figure 9 (a), the forward bias current of the junction diode increased magnificently with the applied bias voltage which indicating the junction diode nature.

Figure 9. (a) I-V characterization for automated p-Zn:CuO/n-Si junction diode (b) Plots ln J vs V for
automated p-Zn:CuO/n-Si junction diode

The current density (J) of the p-Zn:CuO/n-Si junction diode was calculated using thermionic emission (TE) equation as follows which helps to understand the charge distribution mechanism of the fabricated diode [23-25].

\[
I = I_0 \exp \left( \frac{qV}{nK_BT} - 1 \right)
\]

(1)

Where \(I_0\) is reverse saturation current density, \(q\) is electron charge, \(\eta\) is ideality factor, \(K_B\) is Boltzmann constant, \(V\) is applied voltage and \(T\) is absolute temperature. Figure 9 (b) exhibits semi-log plot of the current density (ln J) vs voltage (V) of p-Zn:CuO/n-Si junction diode. The \(\eta\) and \(\phi_b\) has been calculated using following equations [27].

\[
\eta = \frac{q}{K_B T} \frac{dV}{d\ln J}
\]

(2)

\[
\phi_b = \frac{K_B T}{q} \ln \left( \frac{AA'T^2}{J_0} \right)
\]

(3)

where \(A^*\) is a theoretical Richardson constant and \(A\) is active area of prepared diode.

**Table 2. Parameters of p-Zn:CuO/n-Si junction diode under dark and illumination**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>p-Zn:CuO/n-Si junction diode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dark</td>
</tr>
<tr>
<td>Ideality factor ((\eta))</td>
<td>3.32</td>
</tr>
<tr>
<td>Barrier height ((\phi_b)) (eV)</td>
<td>0.686</td>
</tr>
</tbody>
</table>

The ideality factor (\(\eta\)) measurement helps to understand about electron-hole recombination in the fabricated junction diode. The junction diode parameters are shown in table 2. As observed in table 2, the measured \(\eta\) value is 3.32 under the dark condition and the same \(\eta\) value is decreased to 3.19 when the junction diode exposed to light condition. Similarly the measured barrier height (\(\phi_b\)) was found to be decrease under the light condition. The \(\phi_b\) value of the junction diode is 0.686 eV under dark and 0.674 eV under light. The \(\eta\) value of the p-Zn:CuO/n-Si junction diode fabricated by ANSP system is higher than the ideal value of the ideal diode. The result showed that the non-ideal behavior of the p-Zn:CuO/n-Si junction diode. The reason may be owing to the existence of interfacial thin silicon dioxide (SiO₂) between Ag and Si, recombination of current and barrier inhomogeneties.

The ideality factor (\(\eta\)) and barrier height (\(\phi_b\)) values are well in agreement with previous reports which are outlined in table 3. According to table 3 values, Figure 10 shows the comparison graph of the ideality factor and barrier height of p-Zn:CuO/n-Si junction diode with previous reports. As observed in Figure 10, the very lowest value of \(\eta\) and \(\phi_b\) was observed for p-Zn:CuO/n-Si junction diode. The comparison results reveal that the automation system played an important role in the nebulizer spray pyrolysis system. Remarkably, it helps to improve the junction diode properties. Finally, we conclude that automated nebulizer spray pyrolysis system significantly enhanced the p-Zn:CuO/n-Si junction diode property and this system is suitable for thin film deposition and device fabrication.

**Table 3. Comparison of the p-Zn:CuO/n-Si junction diode performance with previous reports**

<table>
<thead>
<tr>
<th>Device structure</th>
<th>Ideality factor ((\eta))</th>
<th>Barrier height ((\phi_b)) (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dark</td>
<td>Light</td>
<td>Dark</td>
</tr>
<tr>
<td>Present work</td>
<td>3.32</td>
<td>3.19</td>
<td>0.686</td>
</tr>
<tr>
<td>Ag/p-CuO/n-Si</td>
<td>5.7</td>
<td>3.5</td>
<td>1.1</td>
</tr>
<tr>
<td>p-CuO/n-Si</td>
<td>6.2</td>
<td>4.6</td>
<td>0.80</td>
</tr>
</tbody>
</table>
Figure 10. Comparison graph of the p-Zn:CuO/n-Si junction diode performance with previous reports (a) ideality factor ($\eta$) (b) barrier height ($\Phi_b$)

4. CONCLUSION

An automated nebulizer spray pyrolysis (ANSP) system is designed and constructed. The mechanical carriage for the X-Y movement and the proposed ANSP system was designed by SolidWorks. Microcontroller based control system was developed to control the X-Y movement of the spray nozzle. p-Zn:CuO/n-Si junction diode is fabricated using this ANSP system. The fabricated p-Zn:CuO/n-Si junction diode parameters were studied under dark and light conditions. The estimated ideality factor ($\eta$) is 3.32 under the dark and 3.19 for light conditions. The obtained $\eta$ value found to be decreased under the light. Similarly, the obtained barrier height ($\Phi_b$) value also found to be decreased under the light condition. The result showed that the non-ideal behavior of the p-Zn:CuO/n-Si junction diode due to $\eta$ value higher than the ideal value. The results reveal that the ANSP system significantly improve the p-Zn:CuO/n-Si junction diode property.

REFERENCES