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Low-Temperature ZnO Thin Film and Its Application in PbS Quantum Dot Solar Cells

Mai Xuan Dzung[1,*], Hoang Quang Bac[1], Dinh Thi Cham[1], Le Quang Trung[1], Nguyen Trong Tung[2], Duong Ngoc Huyen[2], Mai Van Tuan[2,3], Le Dinh Trong[4]

[1]*Department of Chemistry, Hanoi Pedagogical University 2, 32 Nguyen Van Linh, Phuc Yen, Vinh Phuc*

[2]*School of Engineering Physics, Hanoi University of Science and Technology, 1 Dai Co Viet, Hanoi*

[3]*Faculty of Natural Sciences, Electric Power University, 235 Hoang Quoc Viet, Hanoi*

[4]*Department of Physics, Hanoi Pedagogical University 2, 32 Nguyen Van Linh, Phuc Yen, Vinh Phuc*

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Abstract: Zinc oxide (ZnO) has been widely deployed as electron conducting layer in emerging photovoltaics including quantum dot, perovskite and organic solar cells. Reducing the curing temperature of ZnO layer to below 200 ^{o}C is an essential requirement to reduce the cell fabrication cost enabled by large-scale processes such as ink-jet printing, spin coating or roll-roll printing. This paper presents a novel water-based ZnO precursor stabilized with labile NH_3, which allows the spinning of coat crystalline ZnO thin films at a temperature below 200 ^{o}C. Thin film transistors (TFTs) and diode-type quantum dot solar cells (QD SCs) were fabricated with ZnO as electron conduction layer. In the QD SCs, a *p*-type 1,2-ethylenedithiol treated PbS QDs with a bandgap of 1.4 eV, was spin-coated on top of ZnO layer by a layer-by-layer solid state ligand exchange process. Electron mobility of ZnO was about 0.1 $cm^2V^{-1}s^{-1}$ as determined from TFT measurements. Power conversion efficiency of solar cells: FTO/ZnO/PbS/Au-Ag was 3.0% under AM1.5 irradiation conditions. The possibility of deposition of ZnO at low temperatures plays an important role in producing low-cost electronic and optoelectronic devices.

Keywords: ZnO, low-temperature, quantum dot solar cell, TFTs.

1. Introduction

Zinc oxide (ZnO) and titanium oxide (TiO_2) are the most transparent, *n*-type semiconductors deployed in electronics, optoelectronics and photocatalyst. In comparison with TiO_2, ZnO has a lower chemical stability and a shorter electron diffusion length. However, ZnO has a higher electron mobility and, especially it can be processed at much lower temperatures [1]. Therefore, ZnO has been attempted for large-scale and/or flexible optoelectronic devices

*Corresponding author. Tel.: 84-962938394.
Email: xdmai@hpu2.edu.vn

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where low temperature annealing is an essential requirement [2–4].

There are two conventional methods for low-temperature ZnO thin films including sol-gel and sintering of pre-synthesized colloidal ZnO nanoparticles. The later usually suffers from low stability of colloidal dispersion. Sol-gel method is preferredbecause not only it is compatible with solution-based fabrication techniques such as ink-jet printing, roll-roll printing, spray coating and spin coating but also it facilitates varying the chemical composition of final solids. Mixture of Zinc acetate and ethanolamine in 2-methoxyethanol has been deployed widely to fabricate ZnO thin films with annealing temperatures ranging from 200 to 300 ^{o}C[6, 7]. The thermal annealing step that is conducted after solution coating is to induce the condensation reaction between Zn-OH groups and to evaporate organic components such as solvent, ethanolamine and its salts. Herein, we used labile NH_3 to stabilize ZnO clusters in aqueous solution and enabled to reduce the annealing temperature to below 200 ^{o}C. The results must perceive much interests for future flexible electronics and optoelectronics [6, 7].

2. Materials and methods

2.1. Fabrication of ZnO thin films, thin films transistors and quantum dot solar cells

2.1.1. Fabrication of ZnO thin films

$ZnCl_2$ (Semiconducting grade, 99.999 %, Sigma-Aldrich) was dissolved in concentrated NH_4OH solution (28%, Aladdin) at 5 ^{o}C to get a10 weight percent solution, which was stored at 5 ^{o}C in a refrigerator for further uses. Substrates including glasses, quartz, fluorine-doped Tin oxide glasses (FTO) and p-Si^{++}/SiO_2 (thermal growth SiO_2 layer on heavily doped Si wafer) were sequential rinsed with detergent, DI water, ethanol and acetone. Thin films of ZnO on different substrates were fabricated by an identical spin coating method at a speed of 2500 rpm for 50 seconds atroom conditions. The thin films were further annealed at varied temperatures (100, 150, 200^{o}C on a hot plate) for 10 minutes.

2.1.2. Fabrication of thin film transistors

Thin film transistors with ZnO as conducting channel were fabricated by spin coating the ZnO solution onto p-Si^{++}/SiO_2 (thickness of the SiO_2 was 500 Å) substrates, which were pre-patterned with Au-Cr electrodes allowing channels having a width of 1 mm and a length of 10 μm. The coating and annealing procedure was identical to that of ZnO thin films presented above. For TFT measurements, ZnO layer on top of metal electrodes were physically crashed out by a sharp tip.

2.1.3. Fabrication of quantum dot solar cells

The synthesis of oleic acid capped PbS quantum dots (QDs) was carried out using a published protocol [8, 9]. Briefly, a mixture of PbO (4.2 mmol), 1-octadecene (ODE, 18 ml), andoleic acid (OA, 8.4–66.5 mmol) wasdegassed at 120 ^{o}C for 2 hours followed sequentially byadjusting to an elevated temperature, from 65 to 130 ^{o}C, injection ofbis(trimethylsilyl)sulfide (2 mmolin 4 ml ODE), and cooling toroom temperature. The size of the QD was varied by changingtheinjection temperature and/or the amount of added OA. Afterbeing washed once with ethanol andtwice with acetone usingthe typical solvent – non-solvent precipitation procedure, PbSQDswere dispersed in anhydrous n-octane to produce 30 mg/ml stock solution.

PbS quantum dot solar cells (QD SCs) were fabricated by developing a 200 nm-thick, 1,2-ethenedithiol (EDT) treated PbS QDs layer by a layer-by-layer solid state ligand exchange procedure. Briefly, 3 drops of PbS QDs stock solution was poured onto a spinning FTO/ZnO substrate at 2000 rpm followed by dropping 0.3 ml solution of 3 vol% EDT in acetonitrile and then rinsing with acetonitrile to complete one

coating cycle. Thickness of PbS layer increased by about 25 nm for each coating cycle [8]. Finally, the films were transfer into a vacuum deposition chamber to deposit Au-Ag electrodes.

2.2. Characterizations

The crystalline structure of ZnO was investigated by X-ray diffraction pattern conducted on a Bruker D5005 diffractometer. I-V characteristics of TFTs were measure on Agilent B2092A. J-V curves of QD SCs were measure by Keithley 2400. The cells were excited with a Xe lamp 450 W (Newport) calibrated with standard Si cells producing 100 mW/cm^2.

3. Results and discussion

X-ray diffraction patterns of ZnO thin films cured at different annealing temperatures are shown in Figure 1**a**. All ZnO films exhibit diffraction peaks at 2θ of 31.5, 34.5, 36.2, 47.4, 56.5, 62.8 and 68.2 which, respectively, correspond to the diffractions from (100), (002), (101), (102), 110), (103) and (112) planes of ZnO Wurtzite structure (JCPDS-36-1451). The XRD peaks were relatively broad because the ZnO films were thin, about 80-100 nm, and consisted crystalline ZnO nano-sized domains. Clearly, even at low annealing temperature, e.g. 100 ^{o}C, which is boiling point of water, the ZnO film was crystalline.

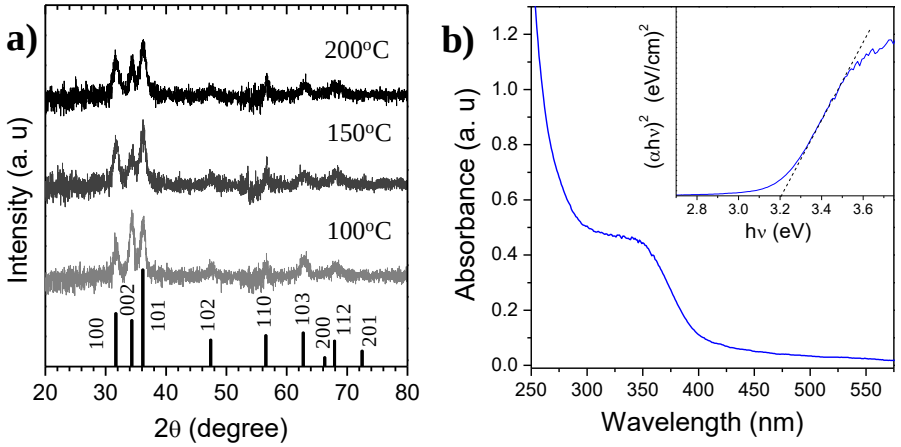

Figure 1.a) X-ray diffraction patterns of ZnO thin films cured at different temperatures and b) UV-vis absorption spectrum of ZnO thin film annealed at 100 ^{o}C.

It has been well documented the formation of ZnO from aqueous $ZnCl_2$ solution via Zinc chloride hydroxyl monohydrate $Zn_5(OH)_8Cl_2.H_2O$ (JC-PDF: 01-077-2311) according to the following reactions.

$$ZnCl_2 + H_2O \rightarrow \left[Zn\ OH\ _{4-x}\ Cl_x\right]^{2-} \quad (1)$$

$$n\left[Zn\ OH\ _{4-x}\ Cl_x\right]^{2-} \xrightarrow{-H_2O} Zn_5\ OH\ _8\ Cl_2 \cdot H_2O \quad (2)$$

$$Zn_5OH_8Cl_2 \cdot H_2O \xrightarrow{>160\ ^oC} ZnO + ZnO \cdot ZnCl_2 \cdot 2H_2O + H_2O \quad (3)$$

$$ZnO \cdot ZnCl_2 \cdot 2H_2O \xrightarrow{>200\ ^oC} Zn\ OH\ )_2 \cdot ZnCl_2 + H_2O \quad (4)$$

$$Zn\ OH\ _2 \cdot ZnCl_2 \xrightarrow{>400\ ^oC} ZnO + HCl \quad (5)$$

The incorporation of Cl^- in zinc complexes as well as zinc intermediates requires as high annealing temperature as 400 ^oC to fully generate ZnO. In the presence of strong base ligand such as NH_3 it replaces Cl^- and even OH^- to form complexes such as $\left[Zn(NH_3)_4\ OH_{\ x}\right]^{(2-x)+}$, which may undergo condensation reaction producing ZnO cluster stabilized by NH_3 ligands like reaction (2). Due to the lack of Cl^- in the ZnO precursor, the removal of NH_3 and water solvent during thermal annealing induces further condensation among ZnO cluster and forming ZnO, thus efficiently reduces the annealing temperature. As shown in Figure 1, an annealing temperature as low as 100 ^oC is sufficient to form crystalline ZnO.

The optical properties of low-T ZnO films are shown in Figure 1 **b**. UV-vis absorption spectrum shows characteristic onset at c.a. 400 nm and a shoulder at about 350 nm. To estimate the bandgap of ZnO, we draw Tauc plot as shown inset in Fig. 1**b**. The bandgap was calculated to be 3.2 eV, which is reasonable for crystalline ZnO.

As mentioned previously, although crystalline ZnO films could be formed at temperature as low as 100^{o}C for electrical applications water has to be eliminated. Therefore, we used annealing temperature of 150^{o}C for TFT and solar cells fabrications.

Electrical properties of low-temperature ZnO (150 ^oC) thin films was studied by TFT and the results are shown in figure 2. Figure 2 shows that the drain current (I_{ds}) increase when the gate voltage (V_g) increase positively, indicating that the low-temperature ZnO is an n-type semiconductor. Linear electron mobility μ_{lin} of ZnO was estimated by using equation: $\mu_{lin} = \frac{\delta I_{ds}}{\delta V_g}\frac{L}{WCV_{ds}}$ where $\frac{\delta I_{ds}}{\delta V_g}$ is the slope of transfer cuver; L and W are the length (10 μm) and the width (1 mm) of the channel; V_{ds} = 5 V is the drain voltage; and C is capacitance $C = \frac{k}{\varepsilon_o d}$ with k, ε_o, d are the dielectric constant of SiO_2 (3.8), vacuum permittivity, and thickness of the SiO_2 dielectric layer (500 Å)[10]. The calculated electron mobility was 0.09 $cm^2V^{-1}s^{-1}$.

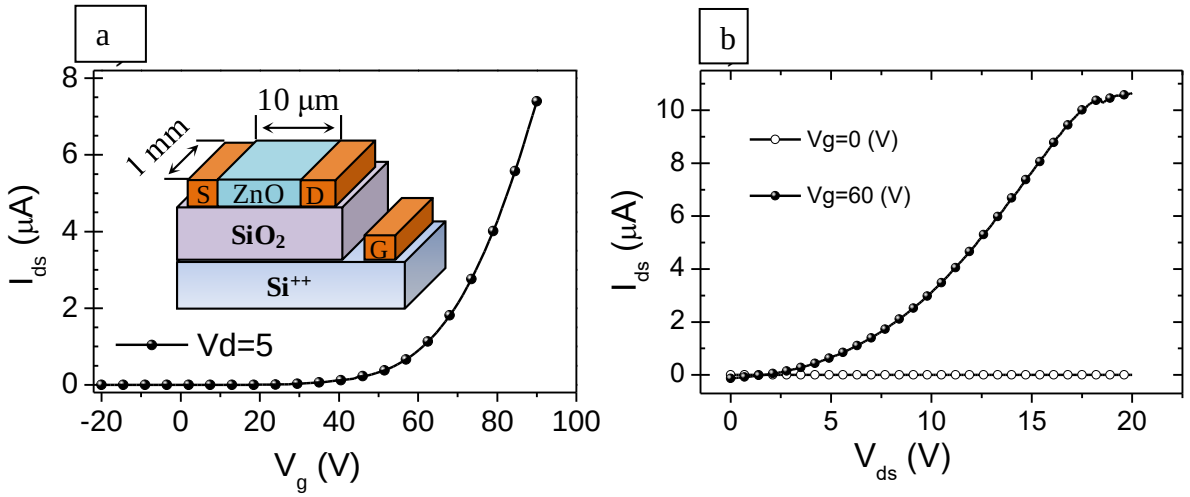

Figure 2. Properties of TFT with ZnO as conducting channel.
a) Transfercurve and b) output curves of ZnO TFT device. Inset in a) is TFT structure.

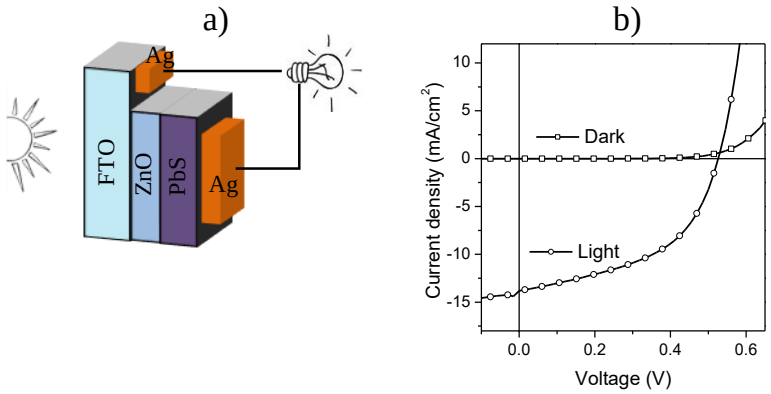

Figure 3. a) Structure and b) J-V characteristics of quantum dot solar cells with ZnO as *n*-type layer.

For comparison, the conventional sol-gel ZnO typically require an annealing temperature above 250 ^{o}C, depending on Zn precursor and stabilizing additives [11]. For example, synthesis of ZnO thin film from mixture of Zinc acetate and monoethanolamine requires annealing temperatures greater than 250^{o}C [12]. These high temperatures are not only to conduct condensation reaction among Zn-OH groups but also to eliminate residual amine additives as well as solvents. In our reaction scheme, labile NH_3 was used to stabilize ZnO cluster in solution state. The easy removal of NH_3 and, probable decomposition of NH_4Cl only need low temperatures, e. g 100 ^{o}C to perform crystalline ZnO films. NH_3 solution has been used previously to dissolve ZnO performing ZnO ink for low-temperature TFTs [13]. Easy volatile NH_3 ligand was discussed to be the key factor to reduce annealing temperature to about 150 ^{o}C. This annealing temperature is still higher than the annealing temperature demonstrated in this study. However, the TFT electron mobility of our low-T ZnO is 0.09 $cm^2V^{-1}s^{-1}$, which is lower than the value reported in reference 13, of about 0.4 $cm^2V^{-1}s^{-1}$ on ZnO annealed at 150 ^{o}C in N_2 atmosphere. It is worthy to note that electron mobility is only one of many physical properties that determine the performance of photoelectronic devices such as solar cells. The other importance factors include trapping density aligning below the conduction band level, energy level of conduction band, carrier concentration, transparency, and carrier diffusion length.

To realize the application potential of low-temperature ZnO in emerging solar cells, we fabricated quantum dot solar cells having structure of FTO/ZnO/PbS/Au-Ag. The structure and J-V characteristics of cell are summarized in Figure 3. For further detail information related to the synthesis of PbS quantum dots, quantum dot thin film fabrications, and electrode deposition, the readers may look at our previous publication [8]. Dark curve of the cell shows negligible current when applied voltage below 0.4 V. This is rectifying property of PbS-ZnO *p-n* junction. Under AM1.5 illumination, the J-V curve shifted down giving rise an open circuit voltage of 0.5 V, a short-circuit current density of 14 $mAcm^{-2}$ and a fill factor of 48%. The corresponding power conversion efficiency was 3.1%.

4. Conclusions

The present study demonstrates the use of NH_3 stabilized ZnO precursor to fabricate ZnO thin films at temperatures below 200 ^{o}C. ZnO films annealed at 150^{o}C exhibits good electron conductivity with a linear mobility of 0.09 $cm^2V^{-1}s^{-1}$ and it is fully compatible with emerging quantum dot solar cells. The possibility of fabrication of ZnO based on

solution process under temperatures below 200^{o}C promise future developments of flexible electronics and optoelectronics.

Acknowledgements

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Màng Mỏng ZnO Nhiệt Độ Thấp và Ứng Dụng Của Nó Trong Pin Mặt Trời Sử Dụng Chấm Lượng Tử PbS

Mai Xuân Dũng[1], Hoàng Quang Bắc[1],
Đinh Thị Châm[1], Lê Quang Trung[1], Nguyễn Trọng Tùng[2]
Dương Ngọc Huyền[2], Mai Văn Tuấn[2,3], Lê Đình Trọng[4]

[1]*Khoa Hóa học, Trường Đại học Sư phạm Hà Nội 2, số 32 Nguyễn Văn Linh, Phúc Yên, Vĩnh Phúc*
[2]*Viện Vật lý Kỹ thuật, Đại học Bách khoa Hà Nội, 1 Đại Cổ Việt, Hà Nội, Việt Nam*
[3]*Khoa Khoa học Tự nhiên, Trường Đại học Điện lực, 235 Hoàng Quốc Việt, Hà Nội, Việt Nam*
[4]*Khoa Vật lý, Trường Đại học Sư phạm Hà Nội 2, 32 Nguyễn Văn Linh, Phúc Yên, Vĩnh Phúc, Việt Nam*

Tóm tắt: Pin mặt trời sử dụng các chất bán dẫn tiềm năng như chấm lượng tử, perovskite và bán dẫn hữu cơ đang ngày được nghiên cứu nhiều hơn với kỳ vọng giảm giá thành và tăng hiệu suất chuyển hóa năng lượng (PCE). ZnO là một trong các oxit kim loại trong suốt được tích hợp rộng rãi trong các loại pin mặt trời trên để làm vật liệu truyền dẫn electron. Do đó, giảm nhiệt độ thiêu kết ZnO là đòi hỏi cốt lõi để có thể chế tạo pin mặt trời giá rẻ bằng cách sử dụng các kỹ thuật chế tạo sử dụng dung dịch như in, phủ quay. Trong bài báo này chúng tôi trình bày một dung dịch tiền chất ZnO mới lạ, bền hóa bởi phối tử dễ bay hơi NH_3 cho phép chế tạo màng ZnO tinh thể ở nhiệt độ dưới 200 ^oC. Transistor và pin mặt trời đã được chế tạo sử dụng ZnO làm lớp dẫn điện tử. Trong pin mặt trời chấm lượng tử, lớp chấp lượng tử PbS với độ rộng vùng cấm là 1,4 eV được phủ quay bên trên lớp ZnO bằng phương pháp trao đổi phối tử pha rắn với 1,2-ethylenedithiol. Nghiên cứu trên transistor cho thấy ZnO có linh độ electron là 0.09 $cm^2V^{-1}s^{-1}$. Hiệu suất làm việc của pin mặt trời chấm lượng tử là 3.0% ở điều kiện chiếu sáng tiêu chuẩn AM1.5. Các kết quả này cho thấy việc chế tạo ZnO ở nhiệt độ thấp cóvai trò quan trọng trong việc chế tạo các thiết bị điện tử và quang điện tử với giá thành thấp.

Từ khóa: ZnO, màng mỏng, pin mặt trời, transitors.