Comparison of APCVD to LPCVD Processes in the Manufacturing of ZnO TCO for Solar Applications

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ABSTRACT

A FirstNano EasyTube 3000 CVD system with a 3" diameter horizontal tube furnace was used to investigate the optimization of both APCVD (Atmospheric Pressure Chemical Vapor Deposition) and LPCVD (Low Pressure Chemical Vapor Deposition) processes to grow both boron and fluorine doped ZnO films with a sheet resistance, slice resistance and haze suitable for their potential utilizations as TCO (Transparent Conductive Oxide) layers for photovoltaic applications. Growth rates as high as 100 nm per minute have been obtained in some parameter regions for both processes. In both cases the resulting material property parameters were the same or better than reported in the literature. Although the horizontal hot wall CVD R&D reactor is not optimum for uniform TCO thin film deposition it allowed us to investigate the interrelationship of the most critical parameters with the resulting material properties.

The driving force for this work is the ultimate goal of demonstrating a process parameter solution suggesting that ZnO films (usable for either display system manufacturing and/or photovoltaic applications) can be deposited with optimized material properties that are comparable to LPCVD or sputtering processes, but that the APCVD solution could be more economical for large scale thin film ZnO coating implementation. Ultimately our desire is to transfer such a ZnO deposition process to our proprietary, APCVD CVDgCoat™ platform, which can coat up to 4 meter wide glass sheets and metal foils that move continuously.

INTRODUCTION

TCO thin films and/or materials typically have low electrical resistivity and high transmittance for visible light. Wide band gap semiconducting metal oxides such as Indium Oxide, Tin Oxide and Zinc Oxide can be doped with suitable amounts of Fluorine or Antimony to improve their conductivity while retaining high transparency. Among them Zinc Oxide has prominent advantages over the other TCOs. This is because, firstly, Zinc precursors are generally non-toxic. Secondly, Zinc materials are less expensive than Tin, Indium or Cadmium. Currently, fluorine doped Tin Oxide (FTO) is the most widely used front electrode for thin film based solar module production. However, FTO can be reduced in hydrogen plasma during Silicon deposition process. The resultant elemental Tin at the silicon interface will cause optical loss and unwanted diffusion, which will lower solar cell efficiency. Zinc Oxide, however, is typically more stable than Tin Oxide in a plasma reducing environment. In addition, it has a higher optical transmittance than the other TCOs. All of the above suggests Zinc Oxide a very promising candidate for solar cell applications [1].

Chemical Vapor Deposition (CVD) processes generally have better deposition rate and uniformity than the other deposition processes such as sputtering and physical vapor deposition (PVD). It is more suitable for large-scale commercial thin film deposition applications. Conductive Zinc Oxide films have been deposited by adding impurity dopant such as Fluorine [2], Boron [3, 4], Aluminum [5-8] and Gallium [9-11]. Three different types of CVD processes, Atmospheric Pressure CVD (APCVD), Low Pressure CVD (LPCVD), and Plasma Enhanced CVD (PECVD), have been investigated for deposition of ZnO layers for solar cell applications and other optoelectronics devices. PECVD is currently in a stage of preliminary investigations [12]. A comprehensive study on APCVD ZnO deposition using different dopant has been conducted by Hu and Gordon [2, 3, 5, 9]. The typical deposition temperature for the APCVD technique is around 400 ^{o}C, which is still quite high for thin-film solar module application. Lowering the pressure allows one to reduce the deposition temperature. LPCVD ZnO growth has therefore been investigated to improve the control of the chemical reactions involved in the deposition process to obtain high coating performance at lower temperature [4, 13, 14].

In this study, the EasyTube 3000 CVD system offered by First Nano, a division of CVD Equipment Corporation, was used to investigate the optimization of both APCVD and LPCVD processes to grow both Boron and Fluorine doped ZnO films with a transparency, sheet/slice resistance and haze suitable for their potential utilizations as TCO layers for photovoltaic applications. The resulting material properties will be characterized and compared with the best properties reported in the open literature. The purpose of this investigation is to demonstrate a process parameter solution suggesting that, by using an APCVD process, ZnO films can be deposited with optimized material properties that are comparable to LPCVD or sputtering processes, the APCVD solution will be more economical for large scale thin film ZnO coating implementation. Our goal is to transfer such a ZnO deposition process to the APCVD *CVDgCoat*™ platform which has the ability to coat up to 4-meter wide glass sheets.

EXPERIMENT

The experiment system for this exploration is shown in Figs. 1 (a)-(d). A customized EasyTube™ 3000's system (Fig. 1a), manufactured by First Nano, a division of CVD Equipment corporation, was used for the experiments reported here. The system houses several key process components including a 3” diameter quartz process chamber, a computer controlled, fully automated process control system for maximum safety and process reproducibility, automatic sample loaders, pumps, a ultra high purity (UHP) gas and vapor delivery system and an EasyGas™ EG600 exhaust treatment system. As shown in Fig. 1(b), the three-zone furnace with cascade control provides better temperature stability and uniformity over a large area. Internal thermal couple measures actual temperature over samples. Furnace lid opens automatically during cooling down stage to save operating time and improve productivity. This versatile system has been adjusted to deposit silicon nano wire, silicon dioxide, SiCxOy [15], APCVD Fluorine doped ZnO and LPCVD Boron doped ZnO successfully. Fig. 1 (c) shows the temperature distribution achieved inside the reaction process tube. Computation Fluid Dynamics (CFD) software, ANSYS FLUENT, is used to conduct the 3-D thermal modeling including conduction, convection and radiation. By applying a constant temperature on the inner wall of the three-zone furnace, it is shown in the figure that a very uniform temperature distribution can be achieved on substrate paddle.

Zinc Oxide films were deposited on three 1cm×1cm bare Silicon (100) substrates and another three 1cm×1cm SiC_xO_y coated soda lime glass substrates by APCVD and LPCVD respectively using the ET 3000 system. The detailed locations of the substrates are shown in Fig. 1(d). Nitrogen was used as the carrier gas for diethyl zinc (DEZ), anhydrous ethanol (for APCVD case) and DI water (for LPCVD case). For LPCVD B: ZnO deposition, Diboran (2 % in high purity Argon, Air Products) was used as dopant and mixed with DEZ in nitrogen carrier gas right before flowing into the injector. DI water was injected separately through another injector. For APCVD F: ZnO growth, Hexafluoropropylene (C_3F_6) was used as fluorine dopant and mixed with the DEZ precursor gas before entering the process tube. Because of the high process temperature for APCVD, ethanol, which is weaker oxidant than water was used as oxygen source (to obtain moderate reaction) and injected separately into the process tube. The typical process conditions used can be found in Table I.

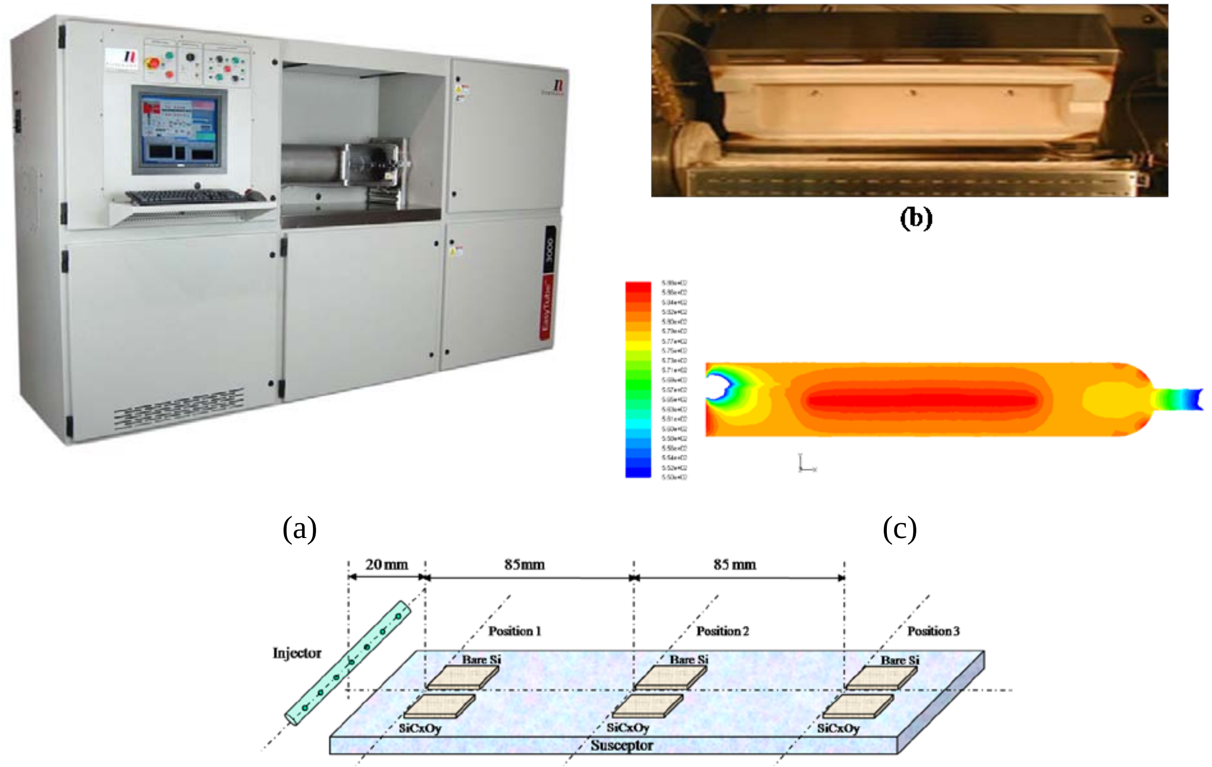


Figure 1: Schematics of (a) ET 3000 system, (b) Three-zone furnace, (c) temperature distribution in the process tube, and (d) over view of sample locations

Table I Typical process conditions for APCVD and LPCVD ZnO deposition

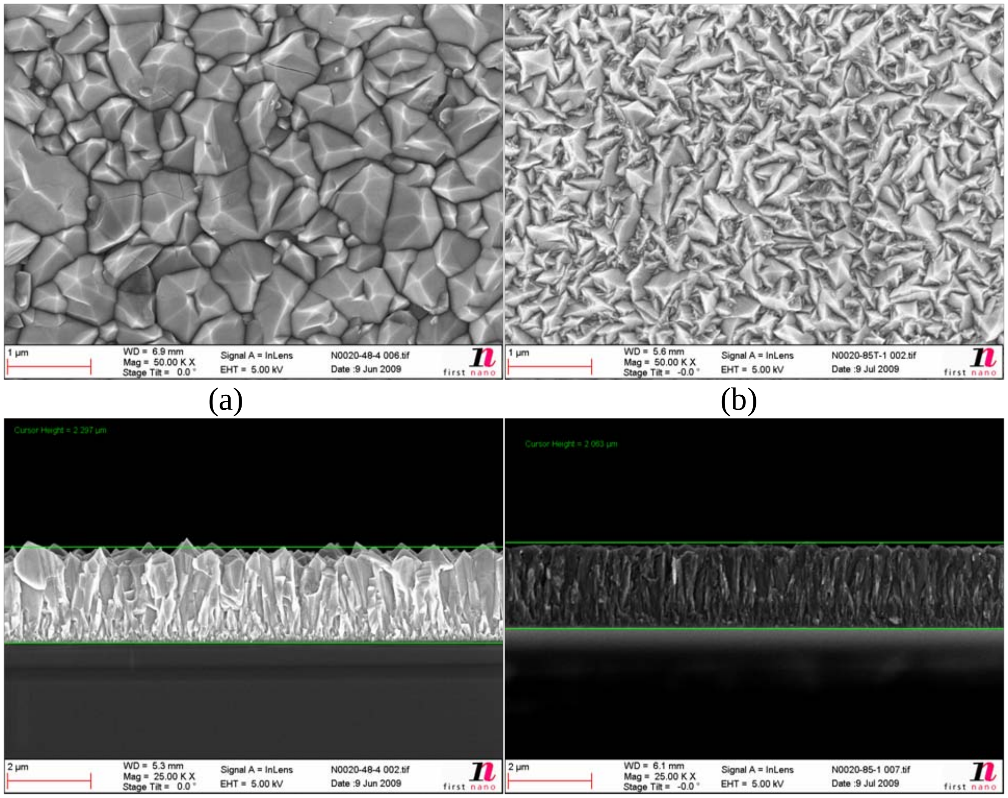
	Reaction Tube		DEZ Bubbler			Ethanol Bubbler			Dopant
APCVD	Temp.	Pressure	Temp.	Pressure	Carrier N_2	Temp.	Pressure	Carrier N_2	C_3F_6
	[C]	[Torr]	[C]	[Torr]	[sccm]	[C]	[Torr]	[sccm]	[sccm]
	375-500	760	25	800 -1000	200 - 400	60	800-1000	200-1000	0-150
	Reaction Tube		**DEZ Bubbler**			**Water Bubbler**			**Dopant**
LPCVD	Temp.	Pressure	Temp.	Pressure	Carrier N_2	Temp.	Pressure	Carrier N_2	B_2H_6
	[C]	[Torr]	[C]	[Torr]	[sccm]	[C]	[Torr]	[sccm]	[sccm]
	140-170	0.3- 0.9	20	300	200-400	25	800-1000	80-200	0-30

Surface topography images have been taken by Scanning Electron Microscopy (SEM) to analyze the surface morphology of the ZnO coatings. Cross-section views were obtained by splitting the Silicon substrate samples to characterize the crystallographic orientation and the microstructure of the ZnO layers. This allowed to measure the coating thickness and to calculate the resulting average deposition rate. The sheet resistance was measured by using a Veeco FPP-100 four point probe. Assuming that the film is homogeneous in the direction perpendicular to the substrate plane, the film slice resistance was deduced from the sheet resistance and coating thickness. The glass transmission and refection were measured by a home-made reflection and transmission measurement setup.

RESULTS & DISCUSSION

Morphology and Microstructure of ZnO from APCVD / LPCVD

Surface topology images for ZnO deposited from APCVD and LPCVD are shown in Fig.2 (a) & (b) respectively. The grain size of ZnO film for LPCVD is smaller than the APCVD ones because of the high deposition temperature for APCVD. Rough surface has been obtained for both cases. Indeed, a rough surface is desirable for solar energy application because it allows the light that enters into the solar cells through the TCO layer to scatter efficiently so as to enhance absorption. Figs.2 (c) & (d) show the cross-section view of ZnO for both APCVD and LPCVD systems. Different crystal orientations and sizes had been obtained for the APCVD and LPCVD process, which agrees well with the observations from other groups [2, 4].



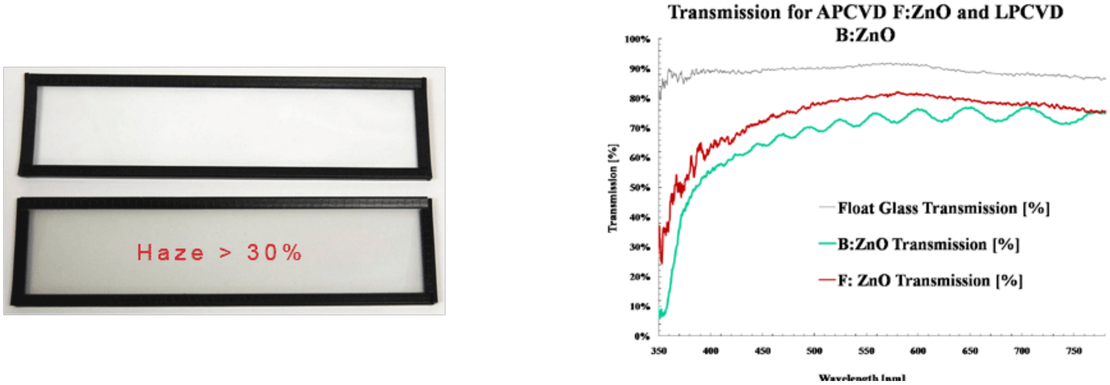
(a) (b)

(c) (d)

Figure 2: SEM for (a) Top view of APCVD F:ZnO, (b) Top view of LPCVD B:ZnO, (c) Cross-section view of APCVD F:ZnO and (d) Cross-section view of LPCVD B:ZnO.

Transmittance, Reflectance and Resistance of APCVD / LPCVD ZnO TCO Films

Figure 3(a) shows that a larger than 30% haze was obtained after a B:ZnO dopped coating was applied on top of the SiCxOy barrier layer coated glass. Surface transmission spectra were also taken to study the optical properties of the obtained ZnO films. The total transmittance of ZnO films with optimized process conditions (deposition temperature, pressure, DEZ/H2O ratio and doping) from APCVD and LPCVD process were shown in Fig. 3 (b). In the case of LPCVD B:ZnO, the film thickness was about 2.5 µm deposited in 15 minutes (with a deposition rate of 160 nm/minute) and the sheet resistance was about 5 Ω/□ with the deduced film slice resistance of 1.3E-3 Ωcm, which is as low as the lowest value for B:ZnO from LPCVD recorded by other groups [4]. The APCVD F:ZnO has a thickness of 750 nm with a sheet resistivity of 11 Ω/□, corresponding to 8.0E-4 Ωcm slice resistance. As shown in Fig. 3 (b) the drop of total transmittance in the blue region for the dopped ZnO was due to free carrier absorption. For solar cell applications, a low optical absorption is desired to allow more photons to enter the active cell region and generate electron-hole pairs. This confirms the importance of minimizing the amount of dopant needed in the ZnO film and optimizing the mobility to lower the resistivity. In our case, 70 to 80% transmission has been obtained for both APCVD and LPCVD cases, which is comparable with results from other researchers and fulfills the requirement for solar cell applications [1, 2 & 4].



(a) (b)

Figure 3: (a) Top view of SiC_xO_y barrier layer coated soda lime glass in frame (upper one) and top view of B:ZnO coating on top of SiC_xO_y barrier layer coated glass (bottom one); (b) Transmission spectra for APCVD F:ZnO and LPCVD B:ZnO coatings on soda lime glass. Deposition conditions for APCVD F:ZnO: growth temperature=400 ^oC, chamber pressure=760 Torr, Ethanol/DEZ mole ratio=8.5, C_3F_6/DEZ mole ratio=0.85. For LPCVD B: ZnO: Growth temperature=160^{o}C, chamber pressure =0.85 Torr, H_2O/DEZ mole ratio=1.2, B_2H_6/DEZ mole ratio=0.03.

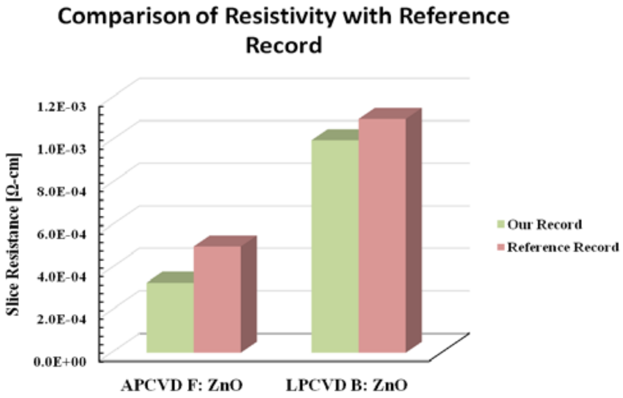


Figure 4: Comparison of resistivity for APCVD and LPCVD ZnO with reference record [1, 2 & 4]. APCVD F:ZnO deposition conditions: growth temperature=400 ^oC, chamber pressure=760 Torr, Ethanol/DEZ mole ratio=8.5, C_3F_6/DEZ mole ratio=0.85. LPCVD B:ZnO deposition conditions: growth temperature=160 ^oC, chamber pressure=0.63 Torr, H_2O/DEZ mole ratio=1.2, B_2H_6/DEZ mole ratio=0.03.

The key factors affecting the coating properties have been theoretically analyzed and experimentally tested for both APCVD and LPCVD ZnO film deposition. These factors includes deposition temperature, chamber pressure, gas velocity, gas Reynolds number, Oxygen source/DEZ mole ratio, Dopant/DEZ mole ratio and deposition time, etc. Based on the theory for design of experiment, various combinations of the factors were further tested to optimize the coating properties. For both APCVD and LPCVD processes, we obtained a respective lower resistance than previously published [1, 2, & 4] despite using the same ET 3000 system. The results and detailed process conditions were shown in Fig. 4. Further investigation for coating properties such as carrier density, hall mobility, dopant concentration, etc. is essential for further optimizing the TCO coating deposition for photovoltaic and solar applications. Integration of the whole investigations will allow us to analyze the interrelationship of the most critical parameters and identify their effects on the resulting material properties.

CONCLUSIONS

In this paper a FirstNano EasyTube 3000 CVD system has been used to deposit F:ZnO and B:ZnO films on Silicon wafer substrates and SiC_xO_y barrier layer coated soda lime glass substrates with both APCVD and LPCVD processes. For both processes, rough surface ZnO coatings had been obtained, which is desirable for solar energy application. High haze factor (larger than 30%) and high deposition rate (higher than 100 nm per minute) were realized for both F:ZnO from APCVD and B:ZnO from LPCVD. A design of experiment study has been conducted for process optimization by using different combinations of key process control parameters in order to achieve a slice resistivity as low as possible for both APCVD and LPCVD processes with good transmittance. For both APCVD and LPCVD processes we report a record-low slice resistivity of 3.0E-04 Ωcm and 1.0E-3 Ωcm, respectively. This investigation provides a promising solution for On-line and Off-line APCVD TCO thin film coating deposition on a very large glass surface area. More follow-up work is necessary to further optimize the process and to transfer such a ZnO deposition process to the APCVD CVDgCoat™ platform which has the ability to coat up to 4-meter wide glass sheets and metal foils moving at high speeds.

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