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

firstnano

Application Laboratory

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ABSTRACT

A First Nano 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 *100nm* 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 which are comparable to LPCVD or sputtering processes. However, the APCVD solution is more economical for large scale thin film ZnO coating implementation. Ultimately, our desire is to transfer such a ZnO deposition process to our proprietary, *CVDgCoat*™ (APCVD) platform, which can coat up to 4m wide glass sheets and metal foils which move continuously.

HIGHLIGHT of EasyTube™ 3000 SYSTEM

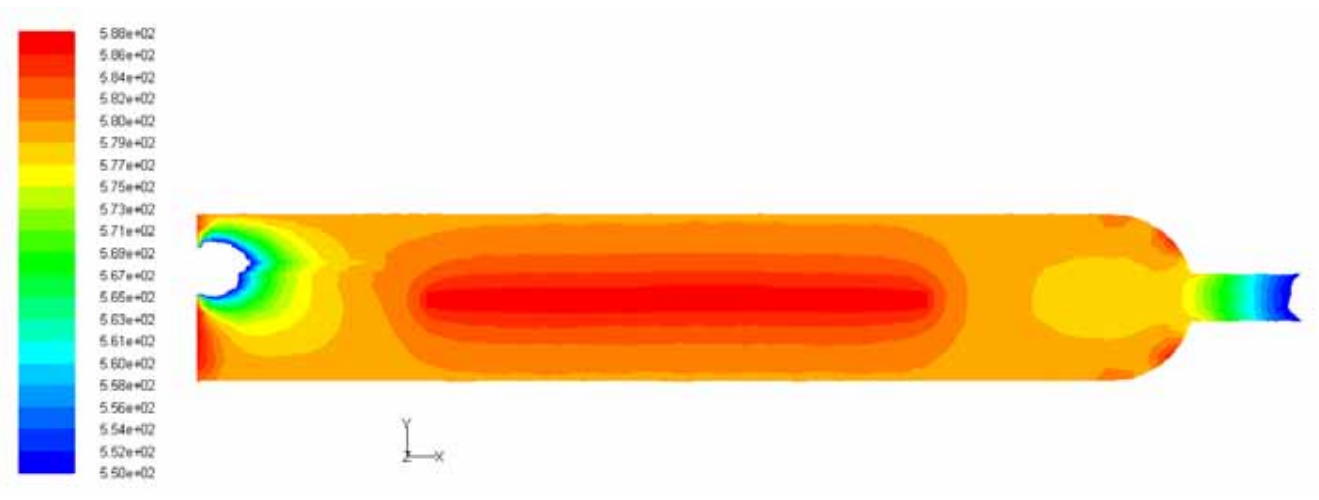
Ø **EasyTube™ 3000** modular platform houses several key process components including a 3" diameter quartz process chamber, a computer controlled, fully automated process control system for maximum safety and process reproducibility, automatic sample loaders, pumps, an ultra high purity (UHP) gas and vapor delivery system and an EasyGas™ 600 exhaust treatment system - all for maximum system flexibility.

Ø **Three-zone furnace** with cascade control provides better temperature stability and uniformity over a large area. Internal thermocouple 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, SiC_xO_y, APCVD Fluorine doped ZnO and LPCVD Boron doped ZnO successfully. Temperature distribution was also numerically predicted 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 highly uniform temperature distribution can be achieved on substrate paddle.

EasyTube™ 3000 System

Three-zone Furnace

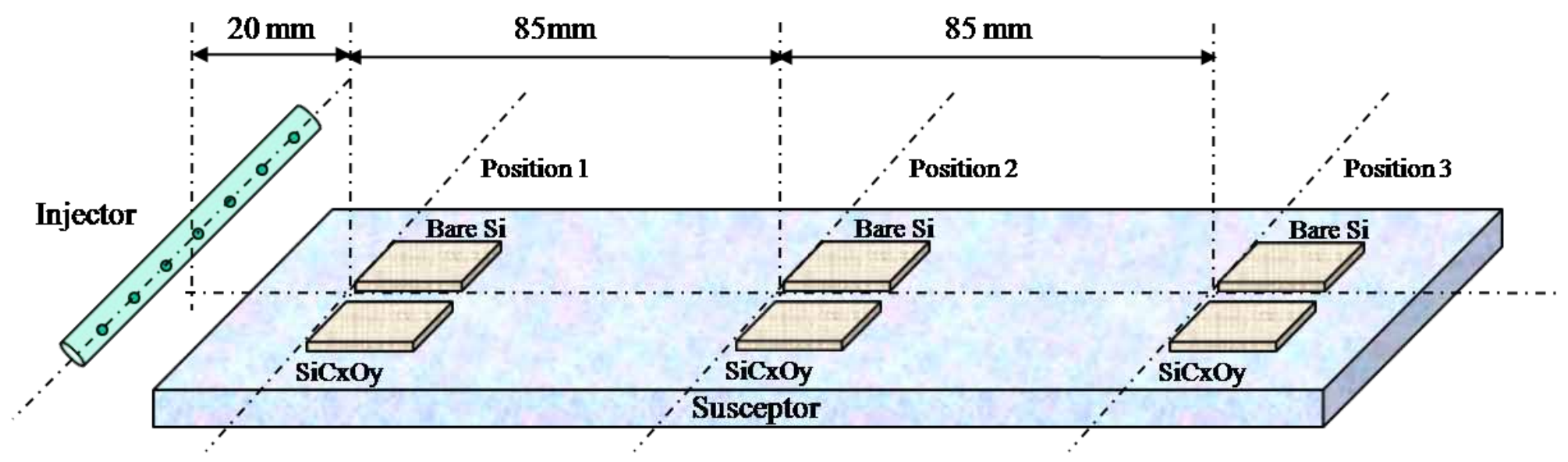
Temperature Profile in Furnace



EXPERIMENT SETUP

Ø**Zinc Oxide** films were deposited on three 1cm x 1cm bare Silicon (100) substrates and another three 1cm x 1cm SiCxOy coated soda lime glass substrates by APCVD and LPCVD respectively using the EasyTube™ 3000 system. 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 Gas Products) was used as dopant. For APCVD F:ZnO growth, Hexafluoropropylene (C3F6) was used as fluorine dopant and mixed with the DEZ precursor gas before entering the process tube.

Overview of Sample Locations



Typical process conditions for APCVD and LPCVD ZnO deposition

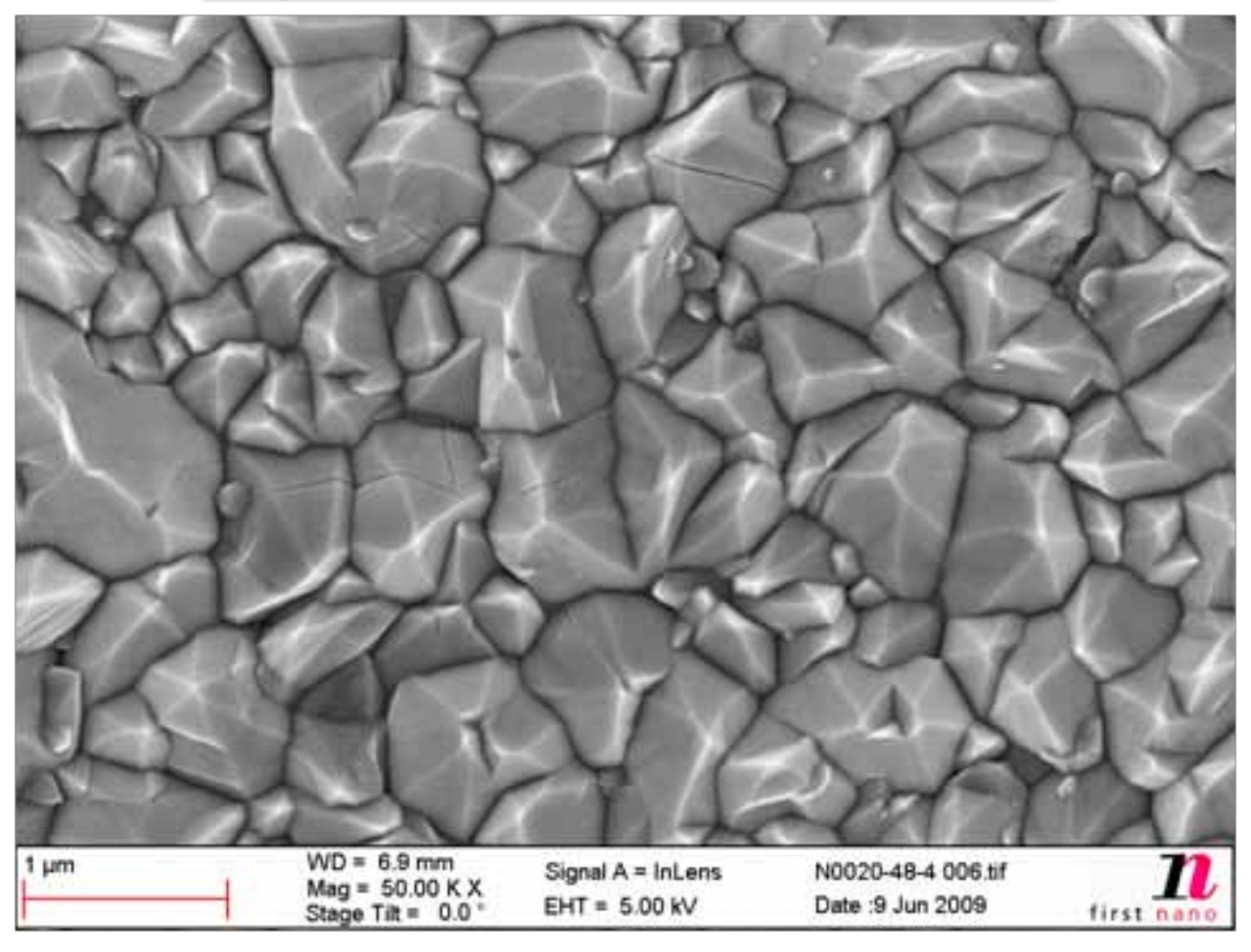
	Reaction Tube		DEZ Bubbler			Ethanol Bubbler			Dopant
APCVD	Temp. *[C]*	Pressure *[Torr]*	Temp. *[C]*	Pressure *[Torr]*	Carrier N_2 *[sccm]*	Temp. *[C]*	Pressure *[Torr]*	Carrier N_2 *[sccm]*	C_3F_6 *[sccm]*
	375-500	760	25	800 -1000	200 - 400	60	800-1000	200-1000	0-150
	Reaction Tube		**DEZ Bubbler**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

RESULTS & DISCUSSION

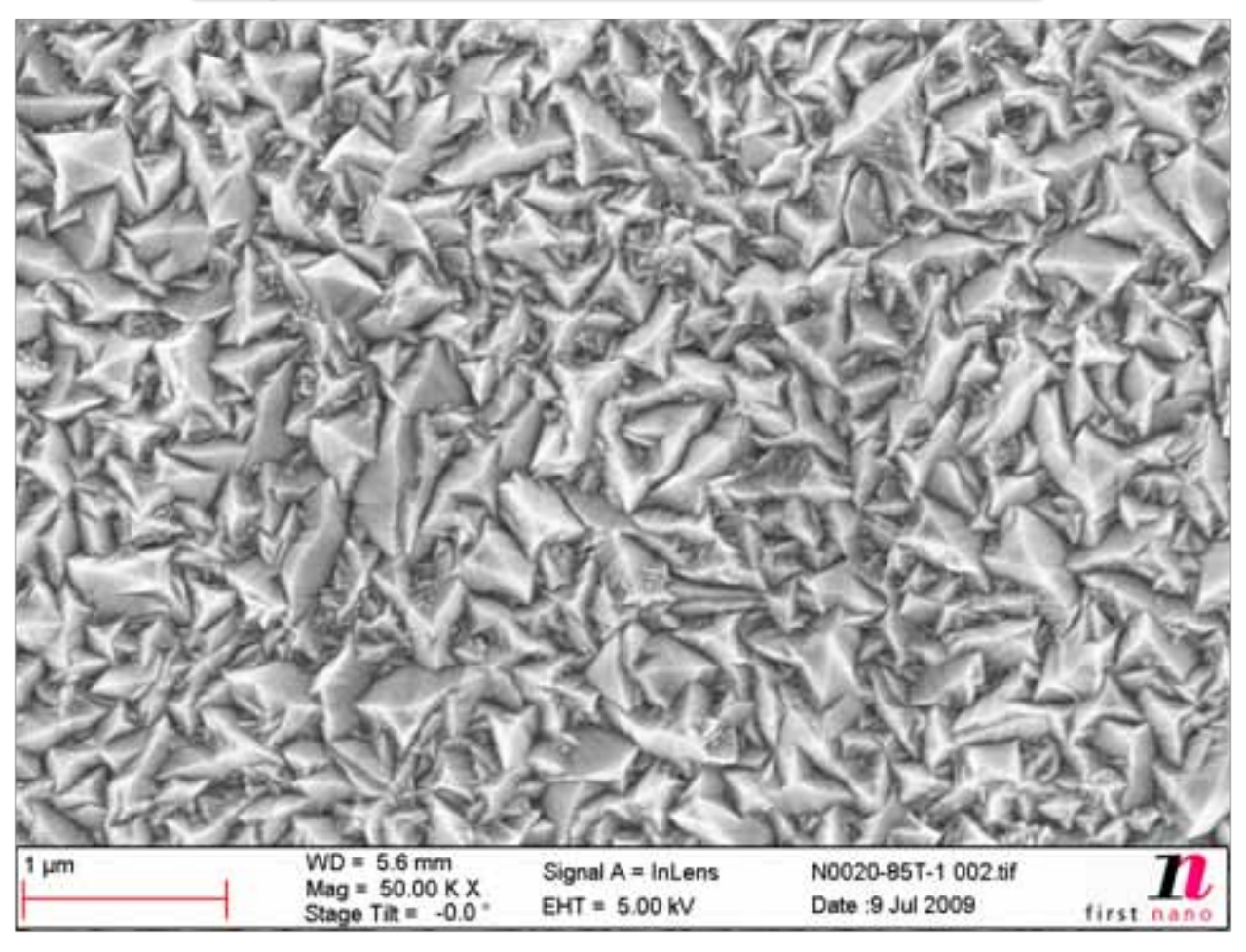
Morphology and Microstructure of ZnO from APCVD / LPCVD

Surface topology micrographs for ZnO deposited from APCVD and LPCVD are shown in the following pictures. The grain size of ZnO film for LPCVD is smaller than APCVD grains due to higher 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. Cross-section views of ZnO for both APCVD and LPCVD systems are also shown here. Different crystal orientations and sizes had been obtained for the APCVD and LPCVD process, which agrees with the observations from other groups.

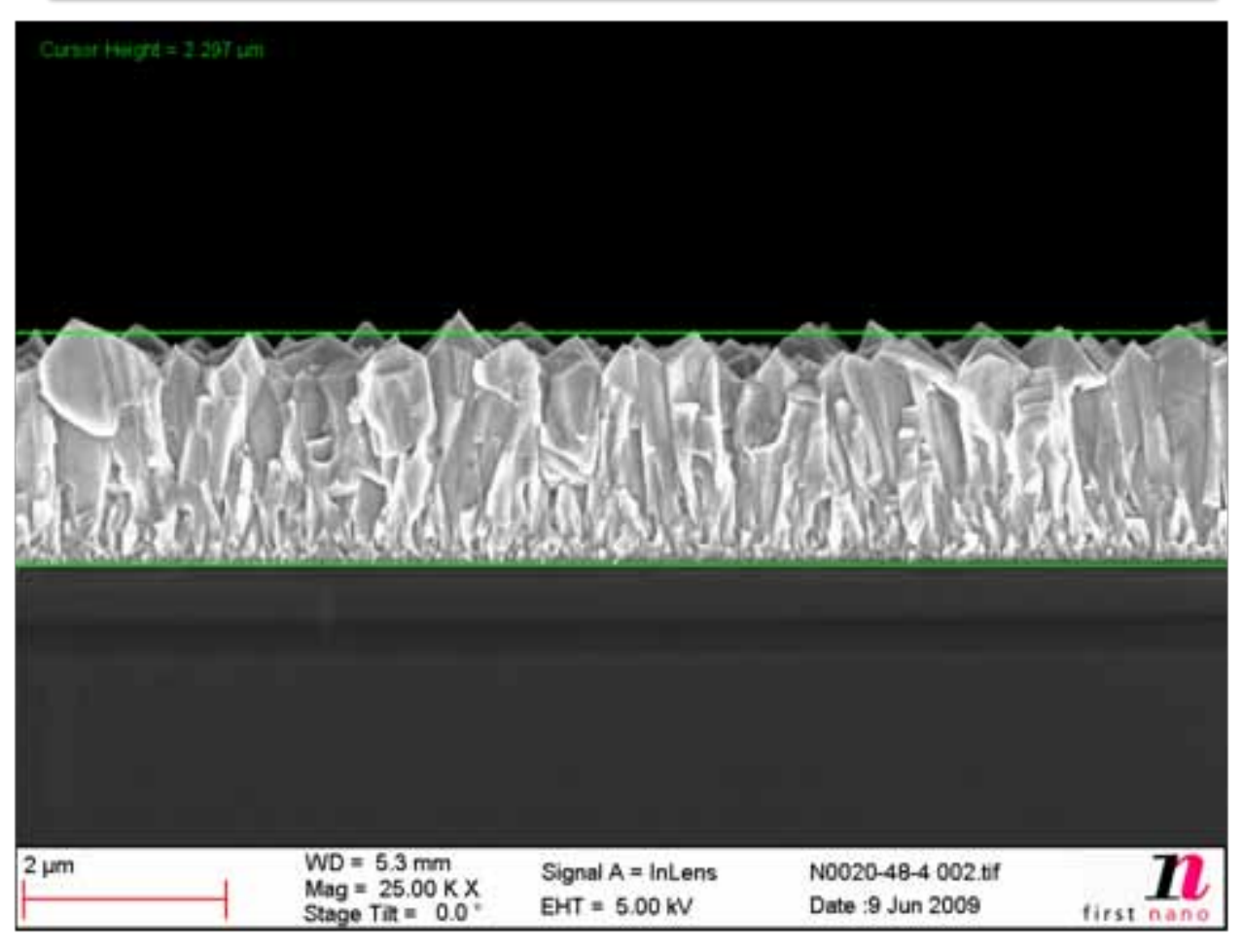
Top View of APCVD F:ZnO



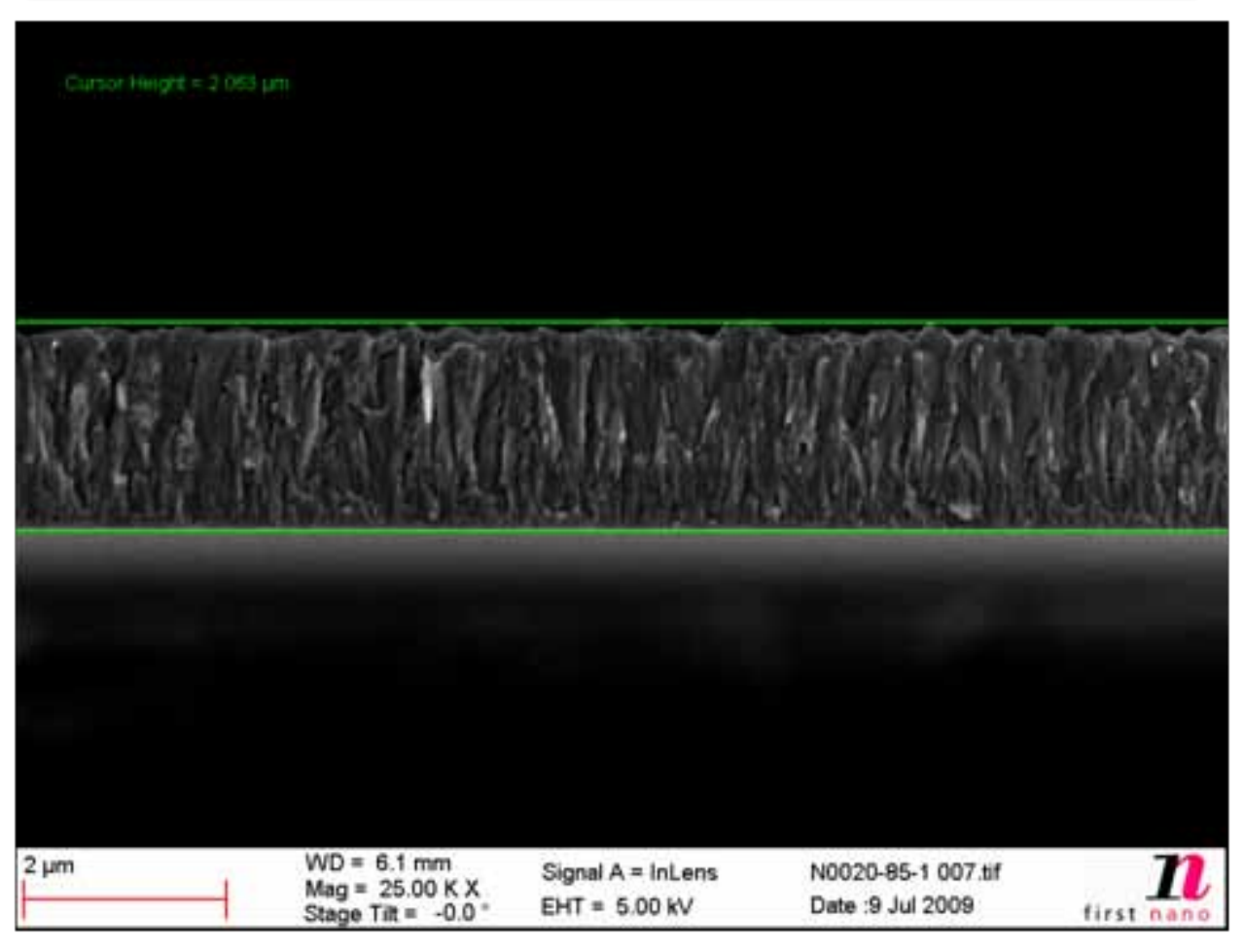
Top View of LPCVD B:ZnO



Cross-section View of APCVD F:ZnO

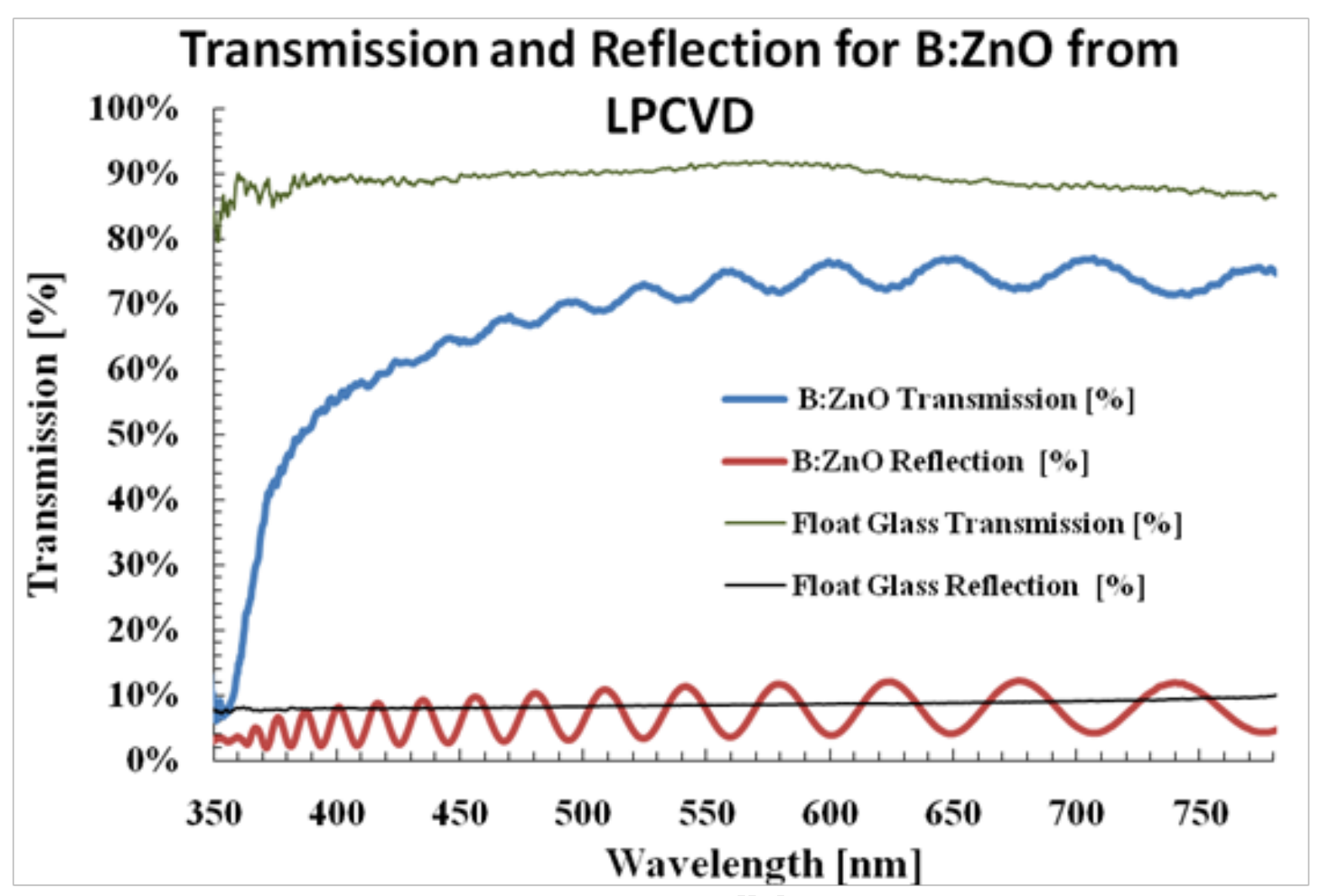


Cross-section View of LPCVD B:ZnO



Transmittance & Reflectance of APCVD / LPCVD ZnO TCO Films

A larger than 30% haze was obtained after a B:ZnO coating was applied on top of the SiCxOy barrier layer coated glass. Surface transmission and reflection spectra were also taken to study the optical properties of the obtained ZnO films. The total transmittance and reflectance of a ZnO film were obtained under optimized process

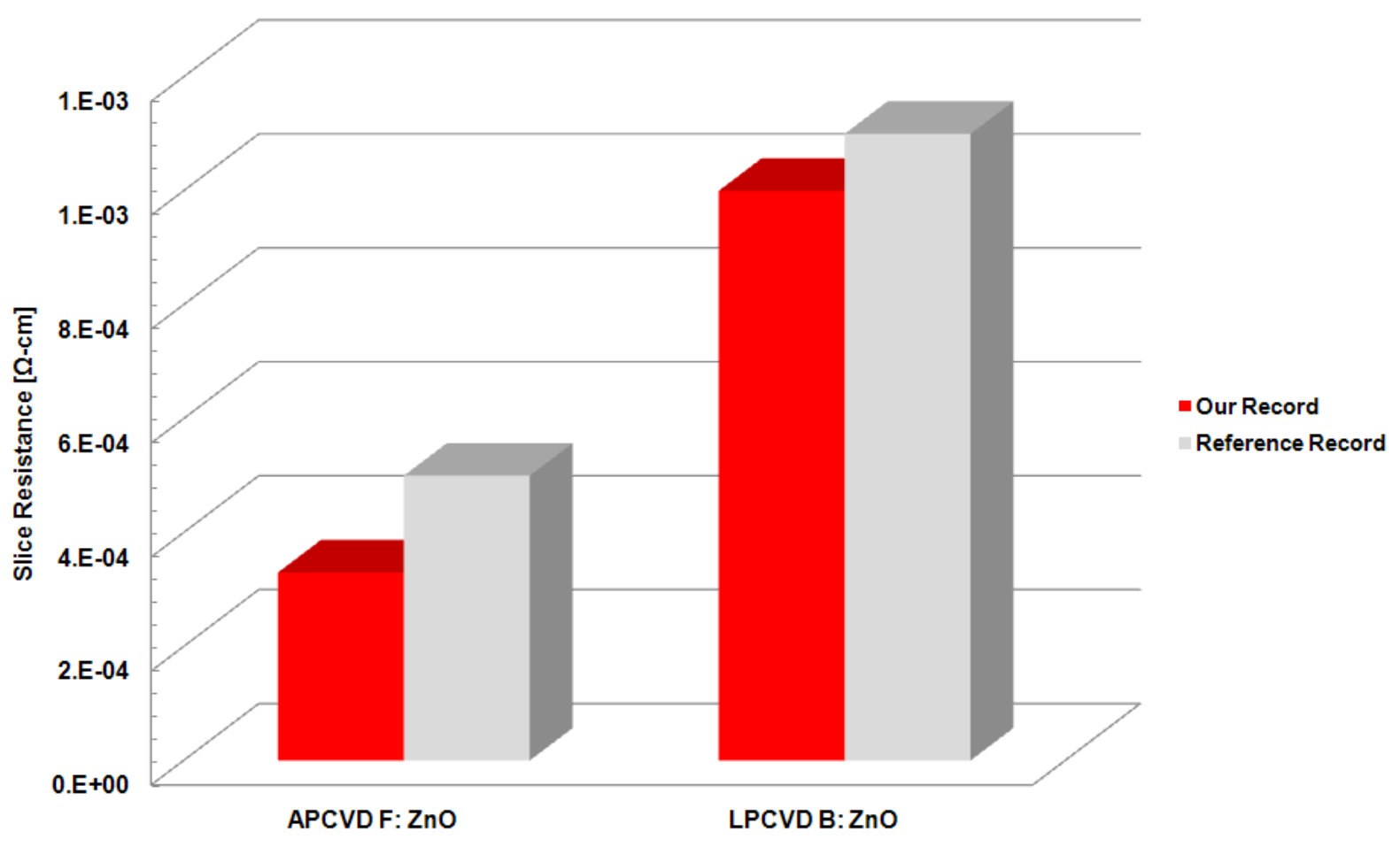


(a) (b)

(a): Top view of SiCxOy barrier layer coated soda lime glass in frame (upper one) and top view of B:ZnO coating on top of SiCxOy barrier layer coated glass (bottom one); (b) Transmission and reflection spectra for B:ZnO coating on soda lime glass. Deposition conditions: Growth temperature=160ºC, chamber pressure =0.85 Torr, H2O/DEZ mole ratio=1.2, B2H6/DEZ mole ratio=0.03, deposition time=15 minutes.

Resistivity of APCVD / LPCVD ZnO TCO Films

The key factors affecting the coating properties have been theoretically analyzed and experimentally tested for both APCVD and LPCVD ZnO film deposition based on the theory for design of experiment. For both APCVD and LPCVD processes, we obtained a respective lower resistance than previously published despite using the same EasyTube™ 3000 system.



Comparison of resistivity for APCVD and LPCVD ZnO with reference record.

APCVD F:ZnO deposition conditions: growth temperature =400ºC, 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 =160ºC, chamber pressure =0.63 Torr, H_2O/DEZ mole ratio=1.2, B_2H_6/DEZ mole ratio=0.03.

CONCLUSIONS

In this paper a First Nano EasyTube™ 3000 CVD system has been used to deposit F:ZnO and B:ZnO films onto Silicon wafer substrates and SiCxOy 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. 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 online and offline 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 CVDgCoat™ (APCVD) platform which has the ability to coat up to 4m wide glass sheets at high speeds.

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