SOLUTION DERIVED NANOCOMPOSITE MATERIALS for PHOTOVOLTAICS

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ABSTRACT

Due to the growing demand for renewable sources of energy, the manufacture of solar cells and photovoltaic arrays has advanced dramatically in recent years. Photovoltaic industry strives to achieve grid parity that requires power conversion efficiency increase and fabrication cost reduction. Light trapping and interface engineering are essential to the performance of photovoltaic (PV) devices. New process technologies can help to drive prices down. [1]

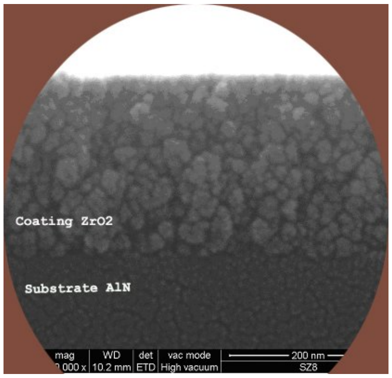
In order to achieve this goal, vacuum methods that are currently used to deposit certain layers during PV-cell manufacturing have to be replaced with more controllable and less expensive techniques.

ADCO Engineering has developed and validated low cost **Solution Derived Nanocomposite (SDN)** coating technology to deliver conformal coatings ensuring enhanced properties. Wet chemistry based thin film deposition routing is proposed to replace high vacuum techniques for several PV critical layers, such as ARC, TCO, BSF and surface modification. Novel approach is capable of placing a conformal film with a perfect adhesion to a substrate, precision control over thickness and stoichiometry uniformity in a very wide range of values, microstructure, and doping level control. It has unprecedented value when ternary or quaternary compound is deposited or interface engineering is performed. The technology is ideally suited

for high level of automation volume manufacturing. This technology is featured by extremely low deposition cost per unit, as it uses no vacuum process tools and plain chemicals and it close to 100% material utilization rate. It can be easily incorporated into solar panels manufacturing lines. [2]

In this paper SDN technology is briefly described with respect to the PV-specific films materials, such as: ***ZnO; CdS; Y_2O_3; Al_2O_3; ZrO_2; SiO_2; SiOC; SiC***. Some of them are currently employed but deposited using another methods and some of them are just coming to play an important role in new cell concept implementation for productivity enhancement and cost reduction. [3] Benefits of SDN technology are discussed for both, crystalline Si and thin film technologies.

SDN TECHNOLOGY OVERVIEW



Our solution of depositing nanocomposite coatings is based upon hybrid sol-gel method - versatile approach for fabrication of binary, ternary or quaternary metal-nonmetal compounds –doped and non-doped.

Solution involves patentable material additives, procedures and deposition equipment that overall determine relationship between properties of the film and other interdependent variables such as processing conditions, precursor formulation and coating thickness and density. Grain and pore size control is possible in a wide range.

SDN technology starts from preparing a coating solution where each and every component is meticulously dosed to ensure a proper stoichiometry in a final product. Doping, catalysts and surfactants are added at this point. Then deposition takes place where the reaction is triggered changing bonding environment that results in a new compound deposited on a substrate. Due to the nature of SDN film formation, deposition and post-deposition processes can control its morphology and properties. As a result, smooth, uniform, continuous, high purity, crack and defect free coatings chemically bonded to substrate with excellent adhesion and desired thickness in the range from 5 nm to 500 um is formed at room temperature and atmospheric pressure. Post-deposition treatment can be applied to modify film's microstructure, e.g. crystallinity, porosity, defect density, etc. Gradient or step case properties' profiles can be created.

SDN is the only technique that allows thorough interface engineering as it provides means to introduce a consequent layer at the various stages of previous one's formation. [4]

Being a derivative of sol-gel technology, SDN is compatible with print, spray, roll-to-roll, dip, spin, and other deposition techniques with a little adjustment to be made to the processing recipe. A wide range of compounds can be fabricated using developed technology. The properties of the films are determined by the formulation and the detailed synthesis procedure, and can be tailored to meet the requirements of specific application. The precursor can be modified with a number of dopants to produce unique properties in the resultant film on the molecular scale unattainable by other coating techniques. Specific organic and inorganic molecules may be incorporated to the matrix, providing new properties. [5]

The technology is ideally suited to high volume manufacturing. It can be easily incorporated into solar panels manufacturing lines; both bulk Si and all kind of thin film PV-devices.

Relative simplicity of compositional and microstructural alteration, formation of crack free relaxed nanocomposite films, versatility to application-specific modifications, conformity to any type of surface finish and geometry, all of these provide an effective method to produce high quality thin films.

SDN technology has several unbeatable advantages over currently used methods:

- Low cost-simple equipment & plain chemicals

- High throughput - no vacuum/high speed line compatible with a conveyer.
- Wide variety of binary, ternary and quaternary compounds with an ultra pure molecular-level control over stoichiometry and doping.
- Defect-free interface engineering
- 2-dimensional structure formation and inter-diffusion.
- Large size substrate-thickness uniformity
- Complex shape-conformal (as opposite to line-of-sight)
- High material utilization-solution recycling - CoC reduction
- Green technology - low energy consumption
- No green house gas emission

PV TECHNOLOGY CHALLENGES and SDN SOLUTIONS

Photovoltaic is in a verge of expansion challenged with the grid parity requirement.

Three generations of solar cell technologies are racing for the better $$/Wp numbers:

c-Si, mc-Si, thin film (a-Si; micromorph; CdTe; CIGS; OPV).

All of them utilize thin film processing in order to form absorber, emitter, light trap-assisting layer, back side field - passivating layer, barriers, windows, metallization, encapsulation, up-converters, etc.

In order to achieve grid parity ($$/Wp) PV technology strives to increase Power Conversion Efficiency (PCE) coupled with reduced Cost of Ownership (CoO). Former is done by optical and electrical losses reduction and implication of advanced interface engineering. Later entails low cost material and technology utilization that justifies industry trend toward innovative methods.

Three key elements in a PV-device define the basis of their manufacturing technology:

- semiconductor that converts absorbed light into exiton.
- semiconductor junction that separates photo-generated carriers.
- contacts to the cell that allow the current to flow to the external circuit.

Two main categories of technology are defined by the choice of the semiconductor:

- silicon in a wafer form (90% market share) or thin film form (3% market share)
- thin films of other materials (7% market share).

Recent expansion of major TF PV manufacturing capacity can cause some changes in these percentages, however, it wouldn't change SDN deployment rate, as both, Si and TF, are prospective users of SDN technology in an exponentially increasing manner.

<u>Si Technology</u> **-** Silicon substrate processing for solar cell fabrication that was mainly inherited from IC-industry, has been receiving further development to address greater plurality of substrate types and device formation specifics.

Two types of substrates are used in the industry:

- **c-Si** (**monocrystalline**) wafers sliced from a high-purity single crystal boule.
- **mc-Si** (**multicrystalline**) wafers made by either sawing of a cast or columnar block of silicon, or growing of a ribbon of Si as a plain two-dimensional strip or an octagonal / dodecagonal column (EFG) by pulling it from a silicon melt and laser wafering. [6]

COO minimization for bulk Si technology entails g/Wp reduction, e.g. substrate thinning, which in turn causes a necessity of several process steps' revision. [7]

Back surface field (BSF) currently is formed as a part of multilayer structure produced during Al-back surface metallization procedure that results in surface recombination velocity (SRV) ~ 10e3 cm/s which is not sufficient for the ultra thin substrates where recombination at the rear surface is getting more critical and, therefore, requires a new approach to creating of advanced passivating layer on a back of the cell. [8]

Implementation of metal doped ceramic compounds (***Y_2O_3, Al_2O_3, ZrO_2***) deposited by SDN will provide not only a superior passivation, but also ensure "no substrate bowing" due to CTE mismatch. The nature of SDN technology allows not generating of built-in or growth stresses as it typical for vacuum methods. Last, but not a least advantage of this technology is that instead of BSF layer where all absorbed photons are gone and not used for conversion, metal doped ceramic compound becomes so-called up-converter layer that converts the low energy photons transmitted by the cell to photons, which are then able to generate additional electron hole pairs when absorbed by the cell, which is illustrated in Table 1 where excitation and emission energy levels of ceramic up-converters layers are shown.

Table 1. Excitation and Emission Values for Y_2O_3 and ZrO_2.

Up-converter	**Excitation range (nm)**	**Emission range (nm)**
Y2O3	**980**	**550**
ZrO2	**980**	**550, 660, 675**

For a side-by-side assessment of PCE increase due to the advanced passivation, several single junction c-Si solar cells have been fabricated using conventional processing.

First group of cells was dedicated to Al-BSF vs. SDN BSF comparison where three types of doping are labeled A, D1, and D2. We observed a substantial improvement in ***Voc*** (Fig.1) and ***Jsc*** (Fig. 2) for SDN-based BSF layer formed by doped ***Al_2O_3, Y_2O_3, ZrO2,*** as providing much better passivation on the back surface thus increasing a minority carriers' lifetime, as well as redextended spectral IQE due to up-conversion of a low energy photons to the ones that are absorbed by the cell and converted into the electrons.

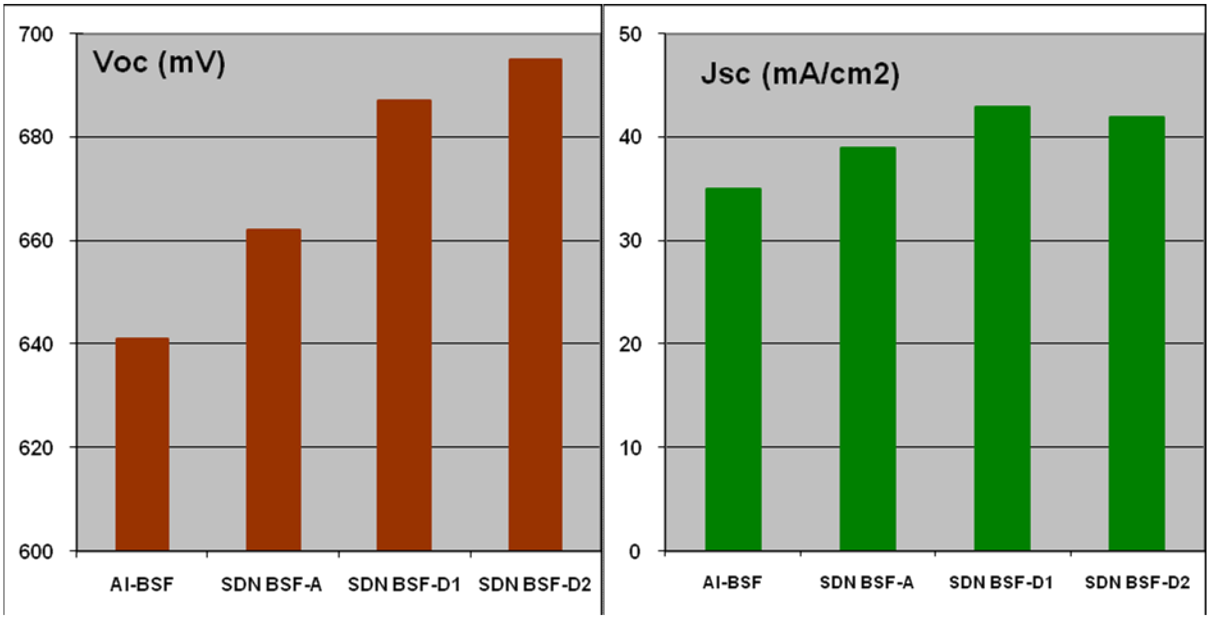


Fig. 1 Voc (a) and Jsc (b) values for various BSF layers

SDN-deposited films help to form better back side contact and back surface field layers that result in overall power conversion efficiency increase.

There was another sub-series of experiments conducted using double layer BSF structure. Double-layer BSF formation methodology that utilizes intermediate ***SiO_2*** sub-layer, exhibited strong correlation between effective surface recombination velocities and ***SiO2/BSF*** films thickness ratios for standard Al-BSF cells whereas SDN BSF seems to be less affected. It is possible that various deposition parameters can influence very different film properties. Unlike thermal or vacuum methods, SDN allows stack interdiffusion at the room temperature.

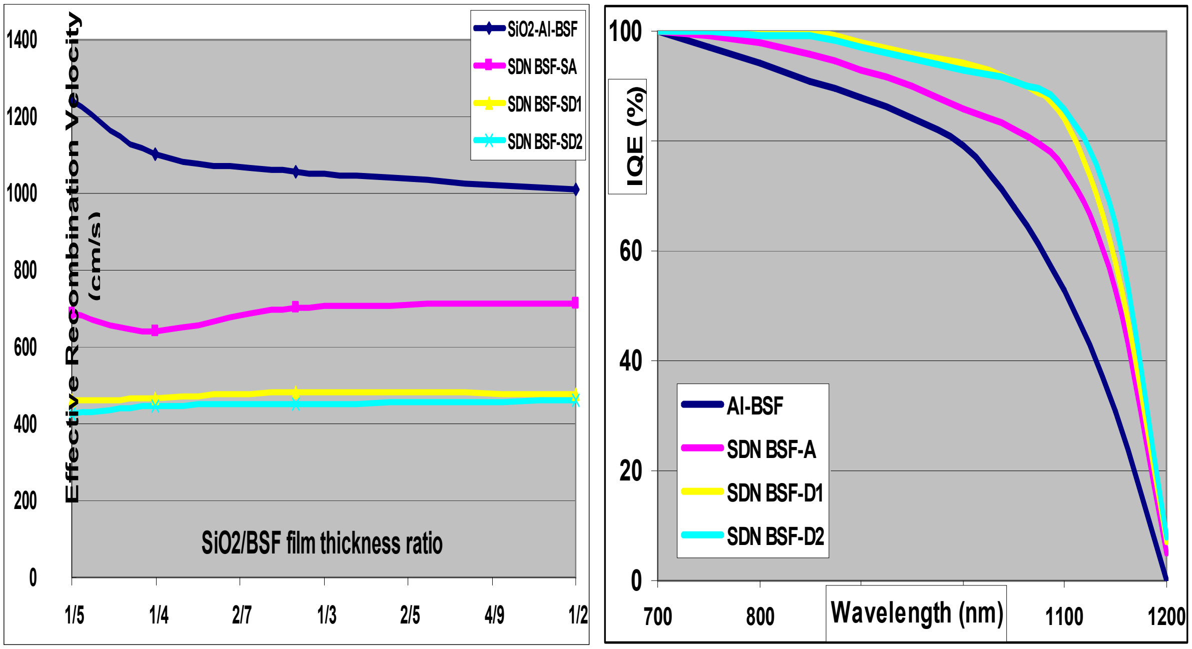


Fig. 2 SRV (a) and IQE (b) for Al-BSF and various SiO2/BSF Ratio

Similarly, additional advantage of SDN-based ***SiO***$_2$ is gained when it is used of the selective emitter formation since (again) SDN is a low temperature process and would not cause any high-temperature associated impact at morphological and microstructural level of the device.

Eliminating of the front grid to increase an amount of light absorbed by the cell is one of the new cell concept features. Creating of interdigitated backside contacts where ***SiC*** passivation layer deposited by SDN provides surface recombination velocities in the range of 10 cm/s is on the PV-technology roadmap.

Moreover, replacing of currently used ***SiOxNy ARC*** that is also acting as a front surface passivation, with ***SiCxNy*** layer deposited by SDN allows reducing spectral reflectivity in a blue range while maintaining very low SRV (Fig. 5).

Important detail is that SDN method is not only substitutes PECVD providing a substantial cost savings but also makes overall PV-cell's manufacturing more environmental friendly and safe, as it doesn't use silane or other toxic or combustible or green house gas emitting compounds.

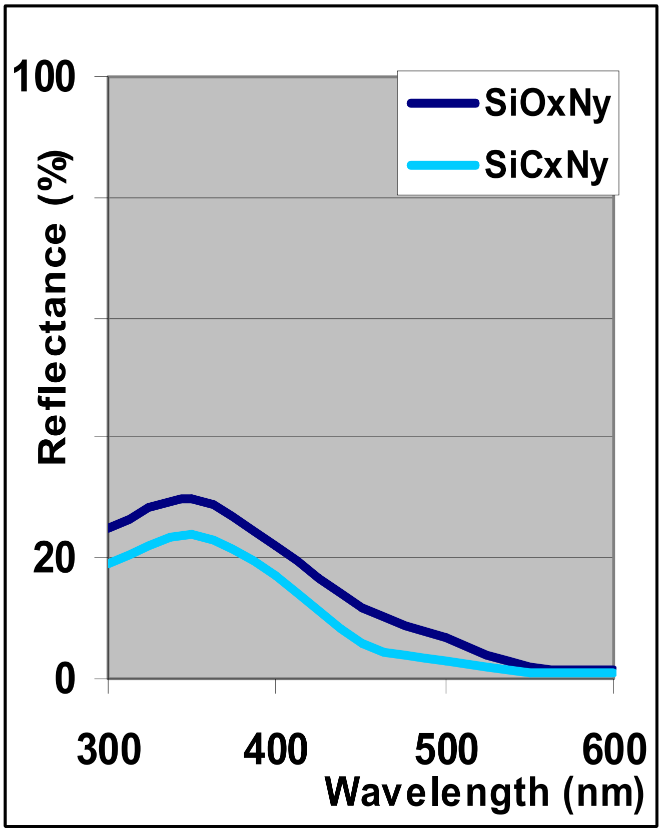


Fig.3. Spectral %R for Standard and SDN Front Passivation

Combining of SDN BSF and SDN ARC is very beneficial for bulk Si-based PV-device performance and productivity enhancement adding up to its' competitive edge. It can bring up to 1.4-1.8% in power conversion efficiency increase and it would also provide at least $0.40/Wp savings by abolishing of vacuum deposition methods.

More opportunity shall be explored as the Si-technology progresses along its roadmap [9]

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Thin Film PV Technology

Thin film PV-development is powered by a desire to have a solar energy converted into the electricity at significantly lower cost than the bulk Si-based products do now.

Four categories of technology (single junction a-Si, multijunction a-Si/mc-Si/ a-SiGe are using different light-absorbing materials with a much in commonality in overall film stack structure.

A. Amorphous Si-based Structures

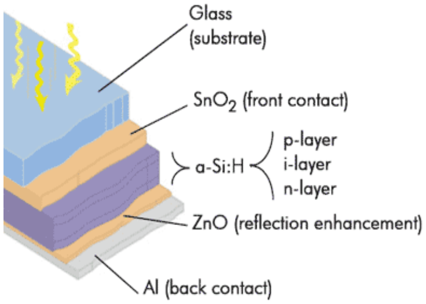


Fig. 4a Single junction a-Si

Amorphous Si-based solar cell is a low cost-low efficiency product that is known for its Staebler-Wronski Effect (SWE) – light induced performance degradation. SWE reduces power output of the module by up to 10%. Using of ZnO and SnO_2 or their combination layers deposited by SDN can reduce SWE impact and improve PCE of the cell by 2-3%

B. Tandem cell a-Si/mc-Si

Tandem cell is comprised out of two semiconductors with the different band gap values that allows of more sun light harvesting and more electron-hole pairs generated.

Top cell/bottom cell thickness ratio defines overall PV-cell power conversion efficiency. Using of ZnO and SnO_2 or their combination layers deposited by SDN can improve PCE by 2-3%

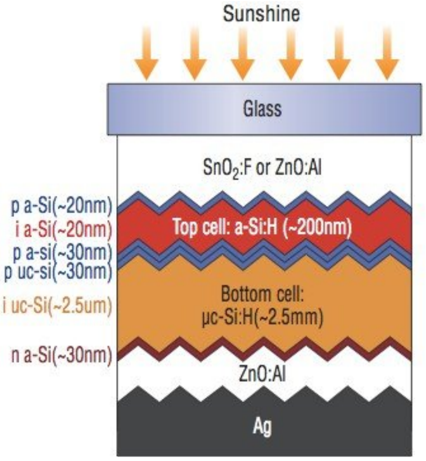


Fig.4b Tandem cell a-Si/mc-Si

BIPV (Building-Integrated Photovoltaics) and consumer products – as well as other lightweight application – all necessitate accelerated development of TF-on flexible substrate-PV devices.

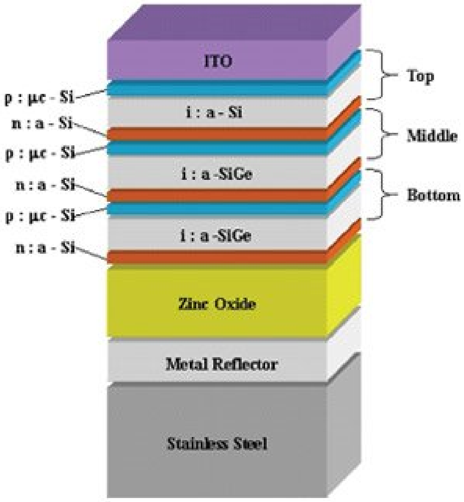


Fig. 4c Triple Junction Ge-doped Si structure

C. a-Si/a-SiGe/a-SiGe triple junction cell

Amorphous cells with different light absorption properties deposited continuously, one on top of another, to capture the broad solar spectrum more effectively. The ability of the cell to absorb different wavelengths of light is defined by modified film stack structure, which also helps stabilizing the cell in regard to the SWE effect. Advanced TCO deposited by SDN can make this design work in terms of manufacturability.

D. CdTe

CdTe exhibits very good characteristics as a thin film photovoltaic material. It has a forbidden gap of 1.45 eV and it is direct. However it grows polycrystalline at T°<500°C and exhibits grain boundaries that limit its efficiency to the relatively low values. Advanced TCO and CdS-window layer deposited by SDN can boost it up significantly.

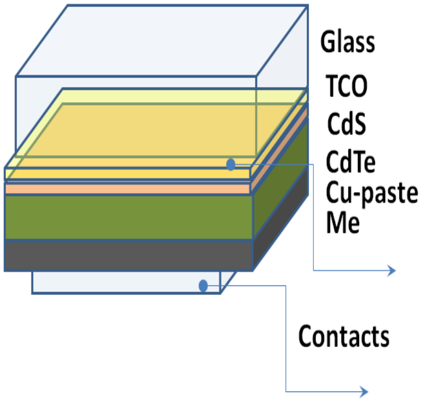


Fig. 5a CdTe-based PV-cell

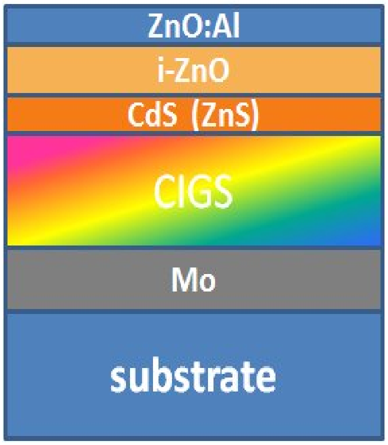


Fig. 5b. CIGS-based structure

E. CIGS - (CIS) - CIGSS

Formation of CIGS-absorber with uniform stoichiometry over the large areas has been a technological challenge lately mainly because of a nature of deposition methods used. SDN can solve this issue providing precision control over basic elements' and doping concentration that along with other films in a stack will enable low cost-high yield process technology.

F. Organic PV

Organic PV technology development has recently achieved its' major milestone [10] when OPV cell with a reasonable efficiency was fabricated using spray coating deposition technique for all layers' deposition. Employing of SDN methodology can bring a substantial enhancement to the power conversion efficiency and reliability of the device.

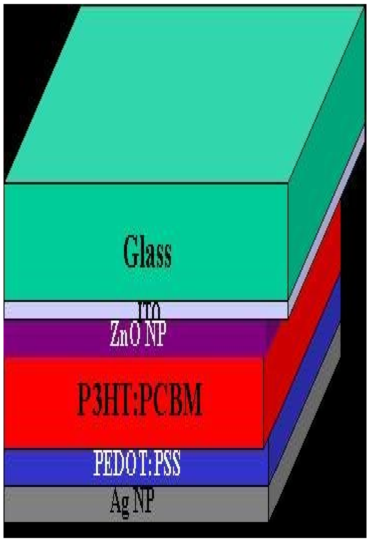


Fig. 5c. OPV cell structure

As indicated on the schematics above, all TF PV technologies make use of ZnO and SnO_2, both intrinsic and doped, as well as a ternary compounds such as Cd_2SnO_4 or Zn_2SnO_4, as a Transparent Conductive Oxides. These materials act as electrodes providing escape passage to the charge carriers, hence their optical and electrical properties per se as well as the quality of their interface with adjacent layers are of utmost importance.

Plurality of PV-manufacturers employs a variety of deposition techniques, which range from molecular beam epitaxy (MBE) through RF Magnetron sputtering to variety of CVD and else.

While all of those serve the purpose of forming a TCO layer, they all are costly vacuum methods using complex equipment with expensive abatement systems. It is particularly challenging to get the right atomic ratio when ternary compounds or compositional gradients are to be created.

SDN provides unmatched capabilities of doing so at a fraction of cost and it is indeed enabling technology for ultra thin or flexible PV-cells fabrication.

Characterization data for Al-doped ZnO demonstrate excellent optical and electrical properties that confirm its suitability to be incorporated into PV-cell manufacturing process flow.

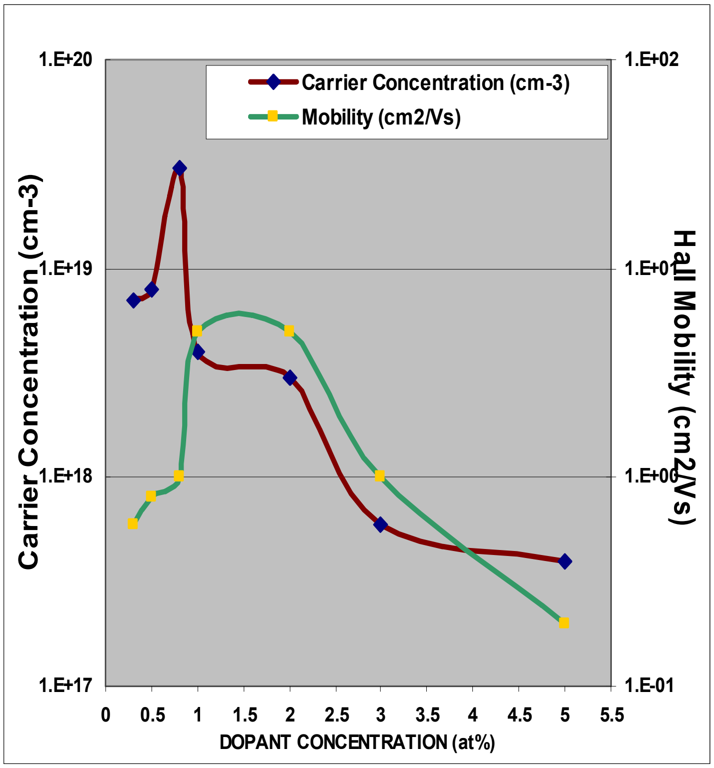
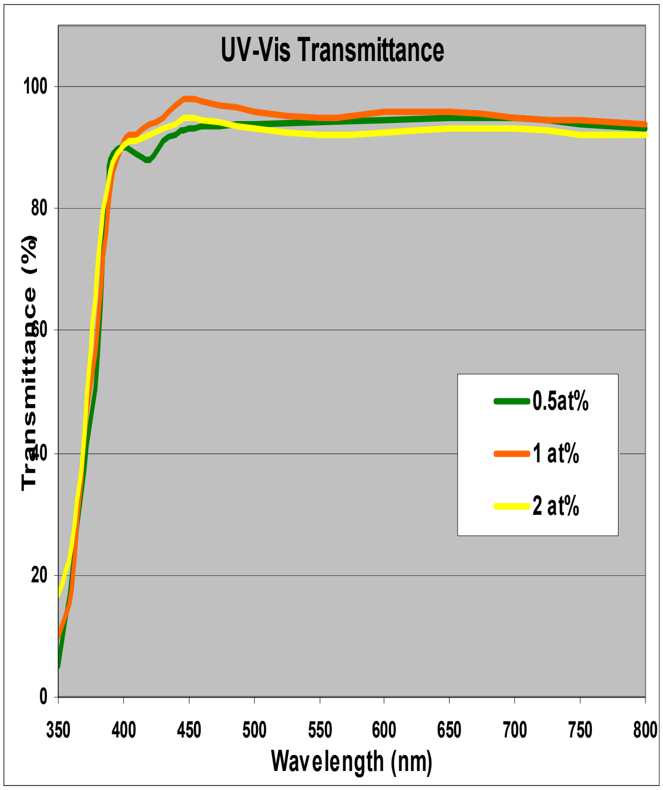


Fig. 6a. Carriers' Mobility and Concentration for ZnO film deposited by SDN

SDN ZnO films (doped and undoped) have been deposited on low cost glass substrates coated with SDN SiO2. Substantial grain size decrease has been observed with Al concentration increase. It is likely that grain boundary is responsible for the decreased mobility in Al-doped ZnO films deposited by SDN.



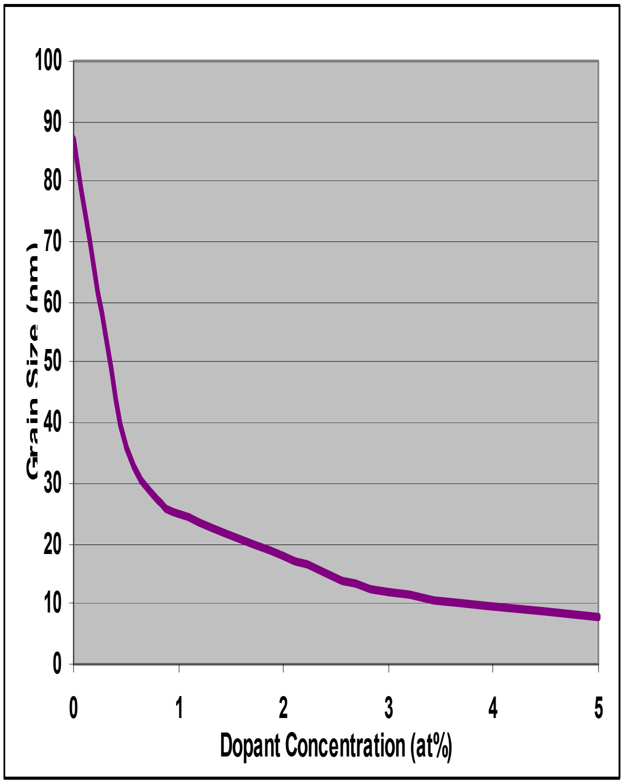


Fig. 6b. Spectral Optical Transmittance for doped ZnO film deposited by SDN

Fig. 6c Grain Size as a Function of Dopant Concentration for ZnO deposited by SDN

Resulting film density is defined by the precision control over process parameters uniformity. Pore size has very narrow distribution.

CONCLUSION

SDN offer very effective way of replacing highly expensive vacuum methods, which also lack ability to comply with ever evolving PV-device structure and fabrication concept. This method is unique in many ways that manifests itself in low cost-high throughput processing of very uniform films in a wide range of thickness and compositional variety.

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