Forming Gradient Multilayer (GML) Nano Films for Photovoltaic and Energy Storage Applications

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ABSTRACT

For successful implementation of the nanomaterial-based PV and Energy storage devices there is a need for well-structured nano films consisting of a strictly controlled sequence of nanoparticle layers. Most promising nano-films include a “built-in” gradient of a nanoparticle size and/or material composition across the part or entire thickness of the film. Such Gradient Multilayer (GML) nano films will be able to significantly improve a PV efficiency of the 3rd generation Solar Cells and Energy storage devices. The development of GML-based devices is presently limited by lack of simple, inexpensive, scalable, and production-worthy deposition methods that are capable of forming GML nano-film on PV-suitable substrates such as flexible materials. The proposed concept describes novel principles of an advanced non-conventional deposition of the highly efficient GML nano films. The proposed GML deposition method is based on the phenomena of Flying Particles (FP). According to the FP-methods a pre-selected mix of nanoparticles (NP) of various size and/or material composition is deposited on a flexible (or other) substrate in a pre-defined order of NP size and/or composition thus forming GML nano film. Deposited GML film comprises a sequence of size-tuned and/or composition-tuned NP layers, which has a potential for significant increase of PV efficiency. The deposition process includes the NPs launch and flight through a resistant gas ambient. Due to the Stokes aerodynamic laws the FP times-to-target will be different for NP of a different size and/or density (material composition). Simulation is presented to confirm the separation of FP’s of a different size and/or density during their motion through the low-pressure gas. The calculations have been made for the initial stages of the FP process thus establishing the most efficient parameters of the process. Resultant GML nano films are expected to have superior qualities, particularly for building high efficiency / low cost PV panels. The FP-method allows for a fast development and easy implementation in PV manufacturing.

INTRODUCTION

From material point of view it is common to consider the following three groups of PV products (i.e. Solar Cells (SC) and Solar Module(SM)): 1) PV products based on well established bulk semiconductors such as Si or III-V group (GaAs or InP-based compositions); 2) Thin Film (TF) SC and SM including most popular a-SiH/a-SiC and CdTe-based structures; 3) Advanced non-standard materials including organic films (polymers), nano crystals (quantum dots, wires etc.), super lattice structures and various combinations of those. The above three groups are commonly referred to as First, Second and Third generations of PV devices respectively.
Both bulk and TF groups of PV products have some fundamental performance and cost limitations that diminish their prospects of being used as an efficient full scale energy sources in the future. In short and simplified form the main limiting factors are described below (PCE stands for Power Conversion Efficiency).

L1. PV performance (PCE) of a single material (or junction) cell is fundamentally limited by the partial utilization of the incoming photon energy combined with the physical limits on photovoltage generated by a cell. For instance, single-junction Si cell can not produce more than 29.5 - 31% of the incoming Sun energy with the best realized numbers of 22-24%. Much lower numbers are typical for CdTe-based, a-SiH and other less expensive TF cells.

L2. Attempts to increase theoretically achievable PCE by using multi-junction (MJ) approach combined with light concentrators, while having multiple advantages, lead to a significant complication of PV system and possible cost increase, reliability concerns are higher too due to the larger number of interfaces, critical layers, heat distribution issues etc.

L3. Generally, cost of materials and processing is high. Availability of a high quality Si represents another important problem. Both bulk and TF products requires “microelectronic” type of processing that includes using high Temperature furnaces, CVD chambers, PVD deposition, patterning technique etc. It makes the average cost of PV energy to be currently at or above $2-3W range with no clear prospects for a significant reduction. The opportunities for increase of the PCE / cost ratio are: a) use of substantially less expensive materials and processes and/or b) use of fundamentally different physical phenomena to achieve much higher PCE.

The alternative nanocomposite and nanostructured materials are currently synthesized by well known colloidal organic process, in gas phase or sputtering. Nanocrystall-based films exhibit some unique material properties highly desirable for PV applications. In short those properties relate to a nanoparticle (NP) capability of better utilization of incoming Light (Solar) Energy by the following:

1) Strong light absorption in the NP-based films due to the light scattering and quantum confinement that allows for making NP-layers extremely thin (10-100nm);
2) Possible energy band “tuning” in a broad range of wavelength by selecting proper material compositions and/or NP size thus widening an available photo active spectral range.
3) possibility for higher PV output voltage (so called Voc) that comes from using distributed NP-based bulk hetero junctions (BH) of Type 2 (staggered band gaps) and separate media for electron and hole transport;
4) Possibility of Multiple Exciton Generation (MEG) in the round shaped NP’s (i.e. Quantum Dots, QD) that may significantly enhance the PCE by full utilization of the incoming photon energy

Unfortunately, the above advantages of NP-based films have been so far difficult to realize mainly due to the conflicts between light absorption, exciton dissociation and carrier transport efficiency. PV results that have been demonstrated so far look modest (low photo current and Voc, PCE at 3-5%, poor reproducibility and reliability); device and process challenges seem to be far from being reliably overcome. Some of the above problems can be solved by using nanostructured layers with the built-in gradient of NP-size and/or material composition i.e. Gradient Multilayer (GML) nano films [1,2].

Unfortunately the existing nanomaterial deposition methods such as e.g. drop-casting or spin-casting technique cannot ensure pre-defined, well controlled GML nano layers. Although a size of a NPs in a film can be well controlled, a proper control over nano structure is impossible to achieve, both composition and NP size wise. Consequently existing nanocomposite PV devices
typically exhibit low carrier transport efficiency (IQE), incomplete spectral coverage, limited Voc etc. More advanced processes, such as ALD or Langmuir-Blodgett methods, on the other hand don't seem to be suitable for a large volume PV production. Based on the above analysis we conclude that although the NP-structured film may lead to a significant PCE/cost improvement the existing methods of depositing nanocomposite films do not have a capability to form GML nano films.

PRINCIPLES OF THE FLYING PARTICLE METHOD FOR FORMING GML NANO FILMS

We propose a novel efficient and inexpensive method of depositing GML nano film on a substrate that provide a pre-defined distribution of NP’s throughout a film in order of their size and / or composition in a single process format. NP’s are assumed to have round shape (Quantum Dots -QD) of a given radius R; composition is defined by the NP materials (e.g. InAs, CdSe, others). The proposed methods form GML nano films on various types of substrates including e.g. conductive flexible substrate of a large area. The pre-defined sequence of NP-layers may be deposited in form of either all-inorganic NP-films or NP’s embedded into a polymer-based films, in both cases the Bulk Heterojunction (BH)-structure of the film is achieved thus ensuring a capability for highly efficient PV energy conversion.

The proposed method of depositing GML layers includes a NP motion through the gaseous ambient toward a substrate, which is placed along the inner surface of a cylindrical chamber prior to the deposition. The proposed method is tentatively called Flying Particles (FP). The essence of the FP method is creating conditions for NP’s of different size and/or compositions to “fly” (NP becomes FP) from a pre-selected NP-source toward a substrate through the selected gaseous ambient.

According to the aerodynamic laws of motion the acceleration of a FP of a given mass is defined by the total force acting upon the particle. For instance acceleration experienced by FP will depend on the instantaneous velocity of a FP, FP’s mass and a FP cross-section area. The latter two are defined of a NP size and density.

According to Newton’s and Stokes’ laws, the motion equation for a small spherical particle in a continuous viscous medium is written as follows:

\[ m \frac{dV}{dt} = -6\pi \mu r \frac{V}{C_p} \]  \hspace{1cm} (1)

where \( m \) is nanoparticle mass, \( \mu \) is gas dynamic viscosity, \( r \) is nanoparticle radius, \( V \) is instantaneous velocity of FP, \( C_p \) is the slip factor, the numerical value of which may be different from "1" for a very small nanoparticle [3]. Noting that \( m = \rho \cdot \frac{4}{3} \cdot \pi \cdot r^3 \) where \( \rho \) is the density of the NP materia, the following equation results from equation 1:

\[ \frac{dV}{dt} = - \frac{K}{(\rho \cdot r^2)} \]  \hspace{1cm} (2)

where \( K \) is the composite factor that reflects specific features of FP motion through the viscous ambient, such as gas pressure, dynamic viscosity, etc.
Equation 2 above shows that for each specific value of the factor $K$, the values of $V$ and $dV/dt$ (which is FP acceleration) strongly depend on both nanoparticle size (radius, $r$) and density, $\rho$. Consequently the time it takes for a given FP to reach the target (substrate surface) positioned at a given distance from the starting point (time-to-target) depends on nanoparticle radius and density, thus providing consecutive deposition of nanoparticle layers in order of size and/or a type of material.

Equation 2 above can be easily solved, and the resulting plots are shown in Fig.1 and Fig.2 for InAs NP flying through the nitrogen ambient. It should be noted that in order to ensure FP arrival to the surface in the normal (orthogonal) direction an electric field can be applied to the space through which FPs fly. In this case, motion equations 1 and 2 need to be slightly modified to include an electrical force. This impact can be used only for a minor correction of the FP trajectory and at this point is not considered significant.

![Fig.1. FP Time-to-Target vs. NP size. NP material is InAs, parameter-nitrogen pressure.](image1)

![Fig.2. FP arrival velocity vs. NP size. NP material is InAs, parameter-nitrogen pressure.](image2)
Analysis of forces and accelerations acting upon FP show that the FP acceleration is a direct function of the NP’s size and/or bulk density (composition) so NP’s of a different size and/or compositions will receive different accelerations during their flight to the substrate. That results in a different time-to-target values for the FPs of a different size and/or compositions and consequent formation of the NP-layers in the order of decreasing size (in the direction away from the substrate) and/or material composition (density). By selecting initial NP mix of pre-defined sizes and compositions the proposed methods will produce a GML nano film with a well-controlled thickness of each NP-layer and pre-defined vertical arrangement of NP’s in the stack according to their size and/or composition.

CHAMBER DESIGN AND PARAMETERS

The chamber for realization of the FP-method can be designed as follows A cylindrical chamber is filled with the low pressure gas (e.g. nitrogen). Transparent flexible substrate with all appropriate optical and conductive coating on it, is placed on the inner walls of the chamber. Pre-selected NP-source may include a colloidal solution containing a mix of NP's of different sizes and compositions, all with pre-selected and well controlled densities. The NP-containing solution is delivered externally onto rotating solid disk or crucible in the center of the chamber

In the beginning of the process the NP colloidal solution is pushed out by a centrifugal force towards the edges of the rotating disk where it is instantly evaporated by a short powerful pulse of the IR- laser. The Nps of the solution remain intact and fly out. During the fly each NP acts as a FP, and an aforementioned discrimination of FP accelerations, velocities and time-to-targets is achieved for the FP’s of a different size and/or composition (density) as described above. That results in gradual depositing NP-structured film on a substrate. Details of the FP method and FP apparatus design are presented in [4].

The above techniques paves the way for synthesizing well-controlled GML nanomaterials with a pre-designed sequence of nanoparticle-based layers. Such materials are expected to provide an enhanced performance of PV, OE and other nano devices.

REFERENCES