An Electrochemical Route towards the Fabrication of Nanostructured Semiconductor Solar Cells

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Abstract – This work presents our preliminary results regarding an electrochemical process which allows the growth of nanostructured materials by means of nanopore templates. Also we analyze possible applications of this process to fabricate nanostructured semiconductors, such as CIGS, suitable for photovoltaic devices, and we consider the implications from the perspective of characterization techniques and device modelling when using such a technology.

Keywords – Solar Cells, Nanostructured Semiconductors, CIGS, Electrochemical Deposition.

I. INTRODUCTION

Copper Indium Gallium Selenide (CIGS) compounds are considered between the most effective materials for solar cells applications. This is due to some advantageous properties, such as high absorption coefficient (1x10⁷ cm⁻¹), adjustable bandgap and optical as well as electronic time stability [1-3]. For such reasons, CIGS based solar cells are considered to be an excellent alternative for polysilicon ones, so that a great effort has been devoted to develop novel devices exploiting this material [4-5]. To date, best performances have been obtained by researchers of NREL (National Renewable Energy Laboratory) which, using a single junction CIGS solar cell (a laboratory-scale device of 0.42 cm² area), reached a conversion efficiency superior to 20% [6]. Such record performances have been attributed to a reduced electron-hole recombination rate at grain boundaries, even though this hypothesis remains under discussion [7-9]. Other authors [10] ascribe the high conversion efficiency to the inhomogeneous composition of CIGS films, which creates local p-n homojunctions not uniformly distributed within the film itself.

The device fabricated at NREL has been obtained by means of a process which cannot easily extended to a larger scale because it requires several vacuum deposition steps, except for the CdS layer formation which can be accomplished chemically. More precisely, the CIGS film was produced with a three-phase co-evaporation that, due to its difficulty, may hamper its commercial exploitation. To make CIGS solar cells more attractive and competitive, it is mandatory to develop a process which turns out to be both cheap and easily extensible to a larger scale. To this aim, electrodeposition can play a key role because it offers these very characteristics, and in comparison with different fabrication techniques, it allows the deposition of good quality CIGS films over large areas [11]. A few years ago it was proposed a hybrid technique, vacuum and electrochemical deposition, for the synthesis of CIGS films which made possible the production of devices featuring an efficiency value of 15.4% [12]. In particular the electrodeposition of a Cu rich film was followed by a chemical vapour deposition step in order to adjust the final stoichiometry. For such a procedure, the role of electrodeposition is of minor importance because the fundamental process remains the vacuum deposition. Actually, the electrodeposition process will become really attractive when it will make possible the direct fabrication of the final product [13]. This issue is one of the obstacles which stand in the way towards the wide diffusion of CIGS solar cells. The difficulty of depositing a film over large areas with the required stoichiometry, that gives rise to poor device yield [14], is due to the complexity of co-electrodepositing 4 elements which have different deposition potentials. Thus, in order to co-electrodeposit Cu, In, Ga and Se it is required to bring closer as possible their deposition potentials, for example by means of suitable complexants, controlling at the same time the kinetics of electrodissolving processes [15-16].

A different possible approach to obtain a compound with a definite stoichiometric fraction of Cu, In, Ga and Se can be that of substituting the aqueous solutions with alcohol based solutions, a method which gives the additional advantage of a reduced hydrogen evolution. Actually, the high reduction potential required for gallium co-deposition, determines a strong hydrogen evolution which can screen the electrode surface so that CIGS deposition is terminated [17].

A major advantage of the electrochemical route for the fabrication of thin film devices, comes from the freedom to create both homo- and hetero-junctions with CIGS. Dharmadasa et al. [18] have shown that homojunctions can be obtained simply by varying the potential applied to the electrolyte solution, considering that this parameter can control both conduction type and band-gap (from 1.1 to 2.2 eV). In particular, at low cathodic potential the deposited
layer is rich in Se and Cu and exhibits a p-type behaviour, while a greater content of In and Ga, which occurs at higher cathodic deposition potential, determines an n-type electric conduction. When considering thin film deposition, the electrodeposition process can produce CIGS with bandgap close to the optimal value of 1.45 eV, which corresponds to almost complete absorption of solar spectrum, thus increasing device performance. Also, by electrodeposition it is possible to fabricate heterojunctions between CIGS and a semiconductor polymer.

Between the several conducting polymers, polypyrrole (PPy) is one of the more studied [19] due to its chemical stability, mechanical properties, and high conductivity, but also because it can be easily obtained by electropolymerization with aqueous solutions containing specific doping agents. Additives such as sulfonic acid and some salts like sulfonated naphthalene or toluene can improve conductivity and adhesion of PPy films [20]. Considering that PPy exhibits a p-type conductivity, by means of the electrodeposition process it is possible to obtain heterojunctions between n-CIGS and p-PPy.

In this complex scenario, one of the most interesting perspectives for research development is that related to technologies which make possible the fabrication of nanostructured materials.

II. ELECTROCHEMICAL GROWTH

A. Electrodeposition of nanostructures

To date, for the best of our knowledge, electrodeposition of CIGS has been investigated only for thin film fabrication, but certainly its extension to the synthesis of nanostructures represents a topic of high interest. In the literature electrochemical techniques have been extensively used for the fabrication of several kinds of nanostructured materials, such as nanowires, nanotubes or nanorods, which in general exhibit very different properties in comparison to bulk counterparts: to name a few, thermodynamic stability, electric conductivity, magnetic and mechanical characteristics. Therefore, these materials can be used for photonics, nanoelectronics and thermoelectronics applications [21-22]. In particular, photovoltaic devices based on nanostructured semiconductors can offer, in comparison to conventional thin film devices, potential advantages such as lower cost, because less material is needed, and higher conversion efficiency. The latter point is related to complex mechanisms such as the increase in photopotential or photocurrent, due to hot carrier or multielectron phenomena which boost light absorption, and to the lack of lattice matching constraints allowed by strain relaxation at the nanowire surfaces [1, 23-30].

On the other hand, all these advantages cannot be exploited without a technique for nanostructure fabrication which can easily scale-up. Also in this case the electrochemical approach offers an ideal path for the synthesis of nanostructured solar cells. In particular, template electrodeposition has been widely tested for the fabrication of several nanomaterials. This is due to its straightforwardness and versatility [34]. Several materials, such as metals, oxides, conducting polymers and semiconductors, can be deposited inside the pores of membranes in polycarbonate or anodic alumina [35-38]. By using this process, nanotubes, nanowires, or nanorods can be obtained with dimensions which can be easily controlled by adjusting template morphology and deposition conditions.

B. Experimental results

For the experiments we used templates made with anodic alumina membranes. These membranes feature an highly ordered porous structure consisting in the regular arrangement of hexagonal cells (similar to the honeycomb structure), each containing a cylindrical pore perpendicular to the surface. In such a structure, a bundle of parallel channels goes through the overall thickness of the membrane, as illustrated in the following Figure 1.

![Figure 1. Ideal arrangement of the porous structure in the anodic alumina membrane.](image)

Fabrication process is based on aluminum anodization, a technique which leads to membranes offering high physical and chemical stability, with different morphology according to experimental parameters: pores have diameter ranging from 20 nm to several hundreds micron, smooth surface, while thickness varies from a few tens of nanometers to a few tens of microns [39]. Pore density is around $10^{22}-10^{13}$ pores/m$^2$ and the degree of porosity ranges from 5 to 30%. Membrane thickness is controlled by total electric charge flow, while morphology depends on the electrolyte nature and on the final anodization voltage. In particular, lowest voltage values correspond to smaller diameter pores, around a few tens of nanometers, while it turns out that with highest voltage values it is possible to obtain pores with some hundreds micron diameter.
C. Semiconductor materials

As a general rule, electrodeposition of solid phases containing more than two elements turns out to be a rather complex process, both because of the different deposition potentials of the various elements, and for the possibility that intermediate phases appear during electrodeposition. In the specific case of CIGS, the complete reaction that occurs at the working electrode surface is:

$$\text{Cu}^{2+} + \text{In}^{3+} + \text{Ga}^{3+} + 2\text{H}_2\text{SeO}_3^- + 8\text{H}^+ = \text{Cu(InGa)}\text{Se}_2 + 6\text{H}_2\text{O} \quad (1)$$

The above reaction is a combination of several processes, having chemical as well as electrochemical nature, that depend on solution pH. The exact CIGS formation mechanism is not yet clear enough, anyway, it depends on the redox potential of each chemical species, on solution composition, and on the applied voltage [17-18]. Furthermore, in comparison to electrodeposition on a flat electrode, specific problems arise from the condition that the process must occur within a confined region like the template channels, which in the case of alumina membranes are about 50 µm deep with a diameter ranging from 20 to 200 nm.

The deposition process was carried out using templates prepared by aluminum anodization in phosphoric acid 0.4 M under a voltage of 160V. Mean pore diameter was found to be about 210 nm, while the thickness was of 60 µm.

Figure 2. Preparation steps of the working electrode (left) and set-up used for electrodeposition (right). (a) Anodic alumina membrane; (b) gold-plating; (c) electrical contact and insulation; (d) deposition inside the pores. (I) Potenziostat; (II) working electrode; (III) reference electrode; (IV) counter electrode.

In Figure 2 we sketch the fabrication procedure of the working electrode and the set-up used for electrodeposition. After a chemical etching of the residual aluminum and of the compact oxide layer which closes the pore bases, we obtain a membrane with parallel channels (a). Before carrying out the electrodeposition, one face of the membrane was sputter-coated with a gold film 150 nm thick (b). After creating electrical contacts and insulation, membrane was immersed in a solution containing Cu, In, Ga and Se ions at different concentrations (d). Specifically, taking into account the different position of the various elements in the galvanic scale, concentrations have been chosen so that cathodic deposition of the less noble species, in our case gallium, is allowed as well. We also investigated the effects of time and applied voltage.

Figure 3. Micrograph of CIGS nanowires after complete etching of the alumina template.

Exploiting the control allowed by the potentiostat it was possible to obtain nanowires containing all four species. Typical composition obtained up to date was Cu_{0.203}In_{0.153}Ga_{0.131}Se_{0.513} which is slightly different to that considered best suited for photovoltaic applications, namely Cu_{0.2}In_{0.2}Ga_{0.2}Se_{0.4}. The above Figure 3 shows a scanning electron microscope picture of the nanowires we obtained, after complete etching of the alumina template. It is clearly seen that wires possess a perfectly cylindrical shape, uniform diameter (about 210 nm, closely matching the mean pore diameter of the alumina template) and a mean height of about 2 µm.

Nevertheless it should be pointed out that even though the fabricated array of nanowires are of amorphous character, they exhibit a cathodic photocurrent (measured for p-type semiconductor) and direct optical transitions corresponding to a 1.54 eV bandgap, much close to the optimal value of 1.45 eV. The photocurrent spectrum, measured in the range from UV to near infrared, of such CIGS nanowires taken at a voltage of -0.7V is given in Figure 4 below.
Figure 4. Photocurrent spectrum of CIGS nanowires taken at a voltage of -0.7V(MSE).

These first results should be regarded as highly interesting, because after a thermal annealing different compositions (related to the high volatility of selenium) are obtained, and also crystal structure modifications which should improve the photocurrent response of such materials. Further investigations are under way to clarify these points, together with the fabrication of p-n junctions and the characterization of the photovoltaic behaviour of the corresponding solar cells.

III. APPLICATION ISSUES

In this section we give a short review of the main points which need to be considered to exploit the developed material for solar cells applications.

A. Fabrication of photovoltaic junctions

As illustrated in previous sections, electrochemical deposition is well suited for the creation of CIGS p-n junctions directly during the growth stage, so that further doping processes are not required. In particular, by varying the applied voltage it is possible to obtain both a p-type behaviour and an n-type, thus creating homojunctions, while with two different solutions it becomes also possible the fabrication of heterojunctions between CIGS and a semiconductor polymer.

B. Device characterization techniques

As well as for conventional cells, characterization in terms of current density and voltage curves (J-V) is of greatest importance [40] because it gives the solar cell conversion efficiency by using a very simple experimental apparatus. Nevertheless, a special significance is related to measuring the current response when varying the incident light wavelength. This latter method actually provides the quantum efficiency (QE) of the device, which strongly depends on structure properties. To further investigate homogeneity of electrical characteristics for the fabricated devices, it is appropriate to complete measurements taken under homogeneous illumination by a solar source at various intensity levels (solar simulator), with those taken both under monochromatic homogeneous illumination from an incoherent source, and with a localized illumination from visible and infrared lasers coupled to a background homogeneous illumination.

This last configuration is known as LBIC (Laser Beam Induced Current), where to an homogeneous level of solar light is also added a laser beam operating in the visible or infrared spectral range [41]. LBIC can be easily carried out and represents a variation of a common local characterization technique for semiconductor devices, namely the Electron Beam Induced Current (EBIC), which would be less appropriate in this case because, on the contrary, it requires a scanning electron microscope and normally cannot be performed under a controlled background illumination [42]. The laser beam is regularly scanned over the active surface of the device and, in a synchronous way, cell electrical response is logged by means of a signal acquisition system, at various laser beam size and intensity. This kind of techniques is of great interest because it allows to map the local electrical properties, which can then be further processed to evaluate important cell parameters while maintaining precise spatial correlation; to name a few: local photocurrent distribution, in-plane diffusion of minority carriers, conductivity distribution and modulation.

Useful references to consider when dealing with solar cell characterization come from those specific IEC International standards which treat thin film solar cell characterization [43-46]. In [43], “procedures for the measurement of current-voltage (J-V) characteristics of photovoltaic devices in natural or simulated sunlight” are described, while in [44], the “requirements for the classification, selection, packaging, marking, calibration and care of reference solar devices” are given. Standard IEC 60904-2:2007 is related to “solar reference devices used to determine the electrical performance of solar cells, modules and arrays under natural and simulated sunlight”. It is worth noting that solar reference devices to be used under concentrated sunlight are not covered therein. In [45] we find prescriptions for design qualification and type approval of thin film terrestrial photovoltaic modules “suitable for long-term operation in moderate open-air climates as defined in IEC 721-2-1”. The latter is meant to be applied mainly to amorphous silicon but it is useful for thin film modules too. Finally, in [46] procedures to correct the “bias error introduced in the testing of a photovoltaic device, caused by the mismatch between the test spectrum and the reference spectrum” are illustrated. In particular, it is considered the computation of...
spectral mismatch error due to both the device under test and the chosen reference.

C. Device modelling

Characterization results are essential to develop a macroscopic model of the nanostructured device. First step approximation is certainly that based on single [47] or double [48] diode circuit models. The latter, even though rarely used, gives a better representation of solar devices which feature non uniform electrical characteristics, and can result more appropriate to describe the functional behaviour of the novel nanostructured devices under study.

IV. CONCLUSIONS

In this paper we presented our first results regarding a process for the electrochemical growth of nanostructured materials, by using nanopore templates. We analyzed possible applications of this process to the fabrication of nanostructured semiconductors suitable for the photovoltaic field, such as CIGS, as well as the implications in terms of characterization techniques and device modelling for devices based on this technology.

Finally, we reviewed the methods used for the optical and electrical characterization of photovoltaic devices based on nanostructured materials, with specific attention to IEC standards applicable to this topic.

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