CHEMICAL AND ELECTROCHEMICAL PROCESSING OF HIGH QUALITY CIS/CIGS ABSORBER, BUFFER, WINDOW, AND ANTI-REFLECTIVE COATING FOR LOW COST PHOTOVOLTAIC TECHNOLOGY

D. Papadimitriou[1],*, G. Roupakas[1], E. Chatzitheodoridis[1], G. Halampalakis[2], S. Tselepis[2],
R. Sáez-Araoz[3], M.-Ch. Lux-Steiner[3], N. H. Nickel[4], S. Alamé[5], P. Vogt[5], M. Kneissl[5]
[1]National Technical University of Athens, [2]Center for Renewable Energy Sources and Saving
[3-4]Helmholtz Zentrum Berlin für Materialien und Energie, [5]Technische Universität Berlin
[1]Heroon Polytechniou 9, 15780 Athens-Greece, [2]19th km Marathonos Ave, 19009 Pikermi-Greece
[3]Institut für Heterogene Materialsysteme, Hahn Meitner-Platz 1, 14109 Berlin, Germany
[4]Institut für Silizium Photovoltaik, Kekuléstrasse 5, 12489 Berlin, Germany
[5]Institut für Festkörperphysik, Hardenbergstr. 36, 10623 Berlin-Germany
*e-mail: dnp.ntua@gmail.com

ABSTRACT: Overall application of inexpensive, non-vacuum chemical (CBD) and electrochemical deposition (ECD) techniques that can be scaled-up to industrial processes is targeted for processing the absorber-, buffer-, and window-layer of CISe/CIGSe TFSCs to overcome current process incompatibilities mainly resulting from the simultaneous use of moderate temperature non-vacuum ($50-70^{o}C$) and high temperature ($500-700^{o}C$) vacuum processes. Low cost ECD processing of ternary $CuInSe_2$ and quaternary $Cu(In,Ga)Se_2$ chalcopyrite semiconductor films with crystal quality similar to that of PVD grown films was achieved by as few as possible process steps skipping selenization at elevated temperatures. Chalcopyrite phase formation was confirmed already in as-deposited films. The film quality was further improved by subsequent annealing at $300^{o}C$, for 2h, in N_2. ZnSe buffer- and ZnO window-layers were processed by CBD and ECD techniques, respectively. The properties of n-ZnO/i-ZnO bilayer were thoroughly investigated with respect to layer thickness and dopant concentration. By successive integration of low cost ECD ZnO/CBD ZnSe buffer and window components in CISe/CIGSe solar cells with absorbers grown by standard vacuum techniques, the respective p-n junctions exhibited I-V characteristics competing with monocrystalline silicon(c-Si) I-V.
Keywords: CIGS; Electrodeposition; Heterojunction; TCO Transparent Conducting Oxides; Metal Contact

1 INTRODUCTION

Solar energy conversion represents one of the most interesting and dynamically growing industry branches. In chalcopyrite semiconductors, high conversion coefficients of the absorber materials, low cost precursors, and low cost processing present an excellent possibility for cost effective energy harvesting with widespread commercialization. A common practice has evolved by alloying lower band-gap $CuInSe_2$ ($Eg \approx 1eV$) with Ga to obtain a $Cu(In,Ga)Se_2$ (CIGSe) quaternary alloy with band-gap raised to the ideal one for photovoltaic cells ($Eg \approx 1.5eV$) [1]. It is essential to employ a heterojunction partner with high band gap towards the light incident side in order to minimize the loss of photogenerated charge carriers. The devices consist of glass/Mo/CIGSe/CdS/i-ZnO/n-ZnO/metal-grid. Highly efficient CIGSe devices [2]-[5] with 20.8% record efficiency [5] were reported so far.

Thin film solar cells (TFSCs) with ternary and quaternary chalcopyrite absorbers are currently being reinforced in view of their efficiency-to-cost prospects. Among various fabrication methods available for the absorber layer, electrochemical deposition (ECD) may be the most effective alternative to the expensive vacuum based techniques. The photovoltaic junction is formed between the p-CIGSe and a combination of a very thin n-type buffer layer (typically CdS) and an n-type wide gap transparent front contact (usually heavily doped ZnO). For high-efficiency CIGS cells, the buffer layer is generally grown by Chemical Bath Deposition (CBD) which is a low-cost, large-area wet chemical process. Electrochemical deposition is not restricted to the deposition of the p-type chalcopyrite film. The preferred TCO (transparent conductive oxide) window of the cell consists of a bilayer of a thin ($\leq 100nm$) ZnO film with lower and a ZnO film with high lateral conductivity (to avoid ohmic losses) which both can be electrochemically

deposited. In ECD/CBD/ECD processing sequence, the whole infrastructure can be implemented in view of wet chemical or electrochemical processes which are significantly cheaper than other deposition methods. Besides, standard CIGSe modules are usually fabricated starting from the back metal contact (molybdenum) and utilizing two or three different growth techniques (vacuum evaporation for the chalcopyrite absorber, chemical bath deposition for the CdS buffer, and vacuum sputtering for the ZnO window), the combination of which makes the industrial production process notably expensive and also suffers from incompatibilities between moderate temperature chemical ($50-70^{o}C$) and high temperature in-vacuum processes ($500-700^{o}C$).

In the present research investigation, wet processing is uniformly employed to process absorber, buffer, window, and antireflective coating (ARC) of ternary (CISe) and quaternary (CIGSe) chalcopyrite based TFSCs. Novel electrodeposition approaches yielding absorber layers with higher degree of crystallinity and sufficient homogeneity in both, composition and morphology, are targeted. Moderate temperatures of deposition and subsequent annealing are expected to limit significantly material interdiffusion at the chalcopyrite - Mo/glass interface and facilitate carrier collection at the back metal contact. Though the CdS buffer layer is very thin (~50nm) and contamination of the environment from CIGSe modules is very unlikely, cadmium is still a hazardous material and its elimination from the module may increase the general acceptance of the product and reduce production costs (by avoiding costly safety measures [1]). Thus, CdS is replaced by ZnSe buffer which is a wide band gap (2.7eV) semiconductor with excellent lattice-match to ZnO window ($a_{ZnO}=3.25Å$, $a_{ZnSe}=3.98Å$) and vast potential for applications in CIGS technology. The ZnO window-layer is deposited by ECD in the form of a bilayer (n-ZnO/i-ZnO) and thoroughly investigated in terms of thickness, dopant type (In, Al),

and dopant concentration. Innovative Antireflective Coatings (ARCs) of ECD grown ZnO nanorod arrays (NRs) are proven to be of excellent optical quality. Sputtered Ag/Ni front metal contacts are found to exhibit lower resistance than Au/Ni and sufficiently lower costs.

2 EXPERIMENTALS, RESULTS AND DISCUSSION

2.1 Chalcopyrite Growth by ECD

Ternary (CuInSe$_2$) and quaternary (Cu(In,Ga)Se$_2$) chalcopyrite selenide thin films were electrochemically deposited on molybdenum/glass substrates 20x15mm^2 from aqueous solution of sulfates, at 70°C, by application of higher negative electrochemical potential Ec=-0.9V, in a standard three-electrode configuration. Details of the deposition process are given in [6]. The thickness of the films was in the range 2.4-3.7µm as calculated from the current versus deposition time (I(t)) characteristics of the electrodeposition process. The deposited films were subjected to subsequent annealing at 300°C, for 2h, in pure N$_2$ atmosphere. The structural properties of the films were analyzed by XRD, SEM/EDAX, RAMAN, and XPS (Fig. 1). The XRD results indicate that CISe films can be deposited, in a single step, by low cost, non-vacuum ECD techniques with quality competing with the quality of expensive, high-vacuum, high-temperature PVD techniques currently applied in processing of commercial chalcopyrite based thin film solar cells. By deposition of quaternary (CIGSe) on ternary (CISe) films near stoichiometric layers (wt% Cu:10.42, In:31.25, Ga:14.58, Se:43.75) are formed. Surface sensitive analysis by XPS confirmed film purity and homogeneity. Except from oxygen and carbon by exposure in atmospheric air, other impurities can be excluded.
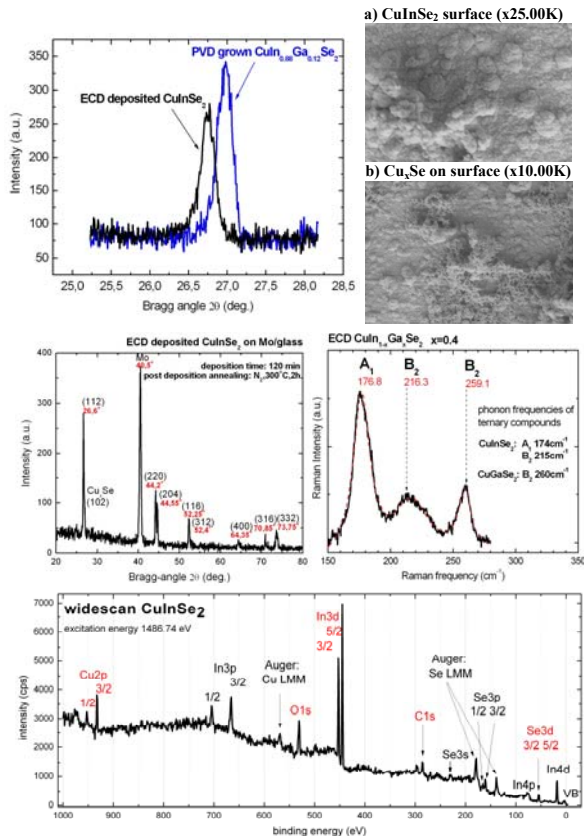
2.2 Growth of ZnSe buffer-layer by CBD

ZnSe thin films were deposited initially on glass substrates and finally on epitaxial and polycrystalline chalcopyrite solar absorbers from ZnSO$_4$ solution with 25% ammonia (NH$_3$) and 25% Hydrazine (NH$_2$NH$_2$) as complexing agents, selenourea (SeC(NH$_2$)$_2$) as selenide precursor and sodium sulfite (Na$_2$SO$_3$) as an antioxidant to initiate the CBD reaction. The bath was maintained at a constant temperature of 70°C. Films deposited on amorphous glass substrates were subjected to subsequent annealing at 300°C, for duration of 1-4h. Films deposited on chalcopyrite absorbers were annealed at 300°C, for 2h, in inert gas (Ar) atmosphere. The films structural and optical properties were analyzed by XRD, SEM/EDAX, AFM and Transmittance Spectroscopy (tauc plots), respectively. Details of growth and characterization are given in [7]. Dependent on substrate (single crystal, polycrystalline, amorphous) and the conditions of growth, ZnSe films can be grown with sphalerite (cubic) or wurzite (hexagonal) structure. On (amorphous) glass and (polycrystalline) chalcopyrite, they were mostly grown with hexagonal structure and exhibited (101) reflection at Bragg angle 29.34^o. On epitaxial chalcopyrite, both the hexagonal and cubic phases were present as evidenced by reflection on (111) crystallographic plane at 27.3^o. After optimization of growth and post-growth annealing processes, high quality ultra thin ZnSe buffer layers of zinc-blende structure were deposited by CBD on Cu(In,Ga)Se$_2$ absorbers as indicated by highly intensive narrow (111) reflection peak at 27.1^o±0.001^o (FWHM: 0.141^o±0.005^o). SEM/EDAX and AFM were applied to analyze composition, morphology, and thickness of the deposited films. The thickness of ultra-thin ZnSe buffer layers was determined by AFM in tapping mode.
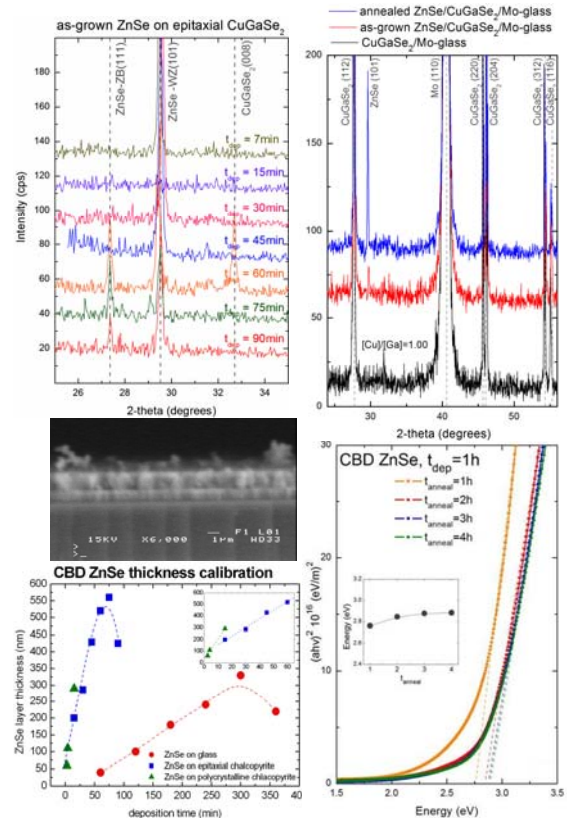

Figure 1: CuInSe$_2$ & Cu(In,Ga)Se$_2$ deposited by single step ECD and analyzed by XRD, SEM/EDAX, RAMAN, XPS.

Figure 2: CBD processed ZnSe films on glass substrates and on epitaxial and polycrystalline chalcopyrite solar absorbers: structure, transparency, and thickness calibration.

2.3 Growth of ZnO window-layer by ECD

Electrodeposition techniques have been also applied to process the ZnO window-layer in the form of a bilayer (n-ZnO/i-ZnO) consisting of intrinsic (i-ZnO) and doped (n-ZnO). The transparent conducting oxide (TCO) serves together with the metallic electron collector as the front contact of CIS (CIGS) cells. Both films were deposited from aqueous solution of zinc nitrate ($Zn(NO_3)_2$) at 80°C and electrochemical potential Ec in the range 0.8-1.2V. Chlorides ($InCl_3$ and $AlCl_3$) were used for doping. The structural and electrical properties of the films were analyzed in dependence of thickness, dopant type, and dopant concentration. Al:ZnO/i-ZnO films on Mo/glass exhibited (101) reflection peak at Bragg angle 38.26°. Scanning electron microscopy (SEM) revealed significant modification of the film structure with variation of dopant concentration in the range 1-20mM. The film thickness deduced from the I(t) characteristics of the deposition process according to Faraday's law (**d**=jMt/nFρ, **j**:charge density, **M**:molecular weight, **t**:deposition time, **ρ**:material density, **F**:96.500, **n**:number of charge transferred) was in best agreement with the results of SEM measurements on the film cross-section. The (electrical) resistance of thicker films was lower possibly because of accumulation of higher (total) number of dopant atoms.
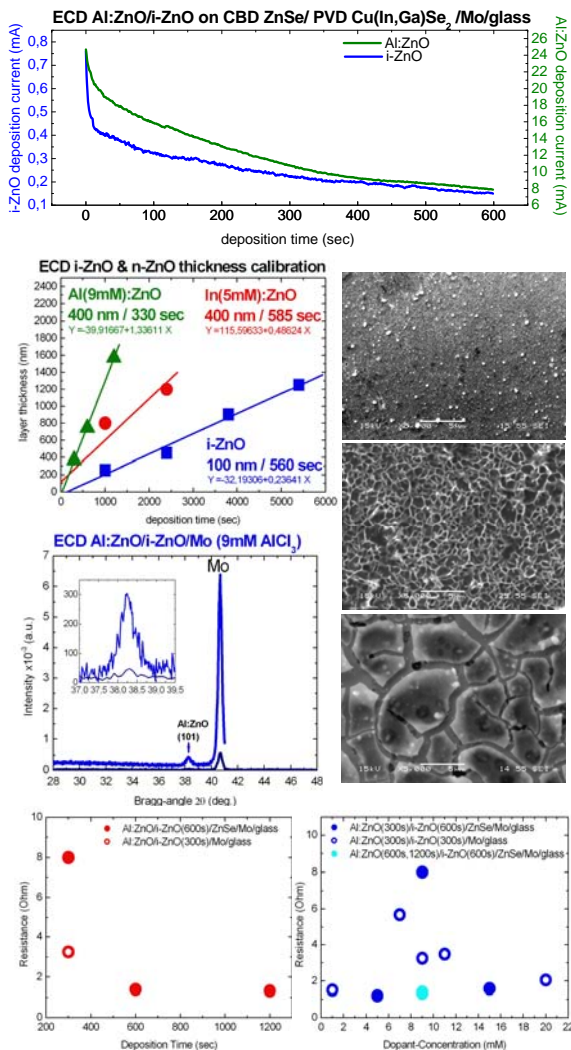

Figure 3: ECD processed n-ZnO/i-ZnO films: structure, resistance, and thickness calibration in dependence of dopant type (In, Al) and concentration.

2.4 Growth of ZnO-nanorod based ARCs by ECD

Innovative Antireflective Coatings (ARCs) based on high quality ZnO nanorod arrays (NRs) were grown by electrochemical techniques initially on transparent conducting oxide coated glass substrates and finally on CIGSe solar cells. The structural and optical properties of the ZnO-NRs were optimized by deposition on intrinsic i-ZnO films (40-50nm thick) electrodeposited on fluorine doped SnO_2-coated glass (FTO glass) from aqueous nitrate solutions at moderate temperature of 75°C. Three different kinds of solutions were used: a) pure $Zn(NO_3)_2$, b) $Zn(NO_3)_2$+HNO_3, and c) $Zn(NO_3)_2$+NH_4NO_3. The samples were characterized by XRD, SEM/EDAX, AFM and Transmittance Spectroscopy. Band gap energies deduced from the tauc plots varied as: 3.32, 3.34, 3.75eV for samples a, b, c. Precise analysis of band energies by Modulation Spectroscopy was given in [7]. The ECD grown ZnO-NRs were truncated hexagonal pyramids with base 150-180nm, apex 40-50nm, height 500nm, and distance between adjacent NRs 200-220nm, which corresponds to a surface packing density in the order of 10^8 NRs/cm^2. Al-doped ZnO-nanorod based ARCs grown in $Zn(NO_3)_2$+HNO_3 bath on CIGSe solar cells lead to a decrease of the weighted global reflectance from 8.6 to 3.5%. Sub-wavelength structured arrays reduce the reflectivity by trapping the incident light likewise to the moth-eye effect.
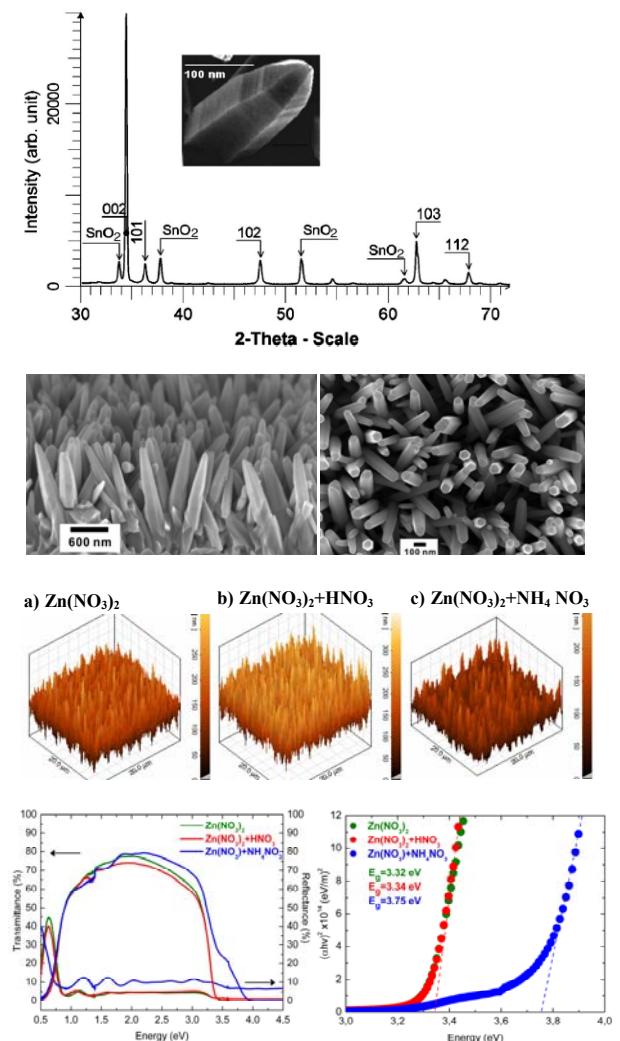

Figure 4: Innovative ZnO nanorod based ARCs processed by ECD: structure and transparency.

2.5 Replacement of Au/Ni front contact by Ag/Ni

CIGS solar cells employ either In_2SnO_3 (ITO) or, more frequently, rf-sputtered Al-doped ZnO as front contact. A combination of an intrinsic (i-ZnO) and an n-doped ZnO (Al:ZnO) layer is commonly used. A grid made of nickel aluminium (Al/Ni) bilayer is selected as carrier collector mainly for laboratory use, e.g. to facilitate contacting the solar cell for characterization purposes. In modules, it is replaced by a more suitable pattern using photolithography and laser printing techniques. In the present work, metal grids of various geometries were sputtered under vacuum conditions or Ar flux. Various metal contacts to p-type CIGSe were examined and Au/Ni was found to ensure an Ohmic contact. Similar results have been reported in [8] for Au/Al contacts deposited on n-ZnO by DC-sputtering and annealed in N_2 ambient. Most profound results, however, gave Ag/Ni apparently because of better matching of the work functions of metal collector and ZnO front contact (Au: 5.1eV, Ni: 5.01eV, Ag: 4.73eV, ZnO: 4.62eV [9]).
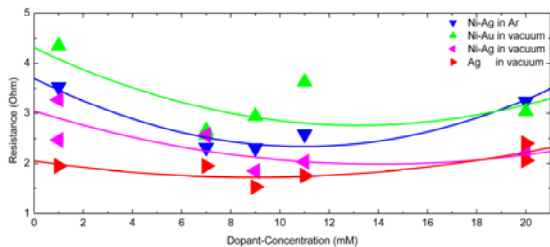

Figure 5: Sputtered front metal contacts in various configurations: electrical properties.

3   CONCLUSIVE REMARKS:
I-V CHARACTERISTICS of Au/ECD In:ZnO/i-ZnO /CBD ZnSe/PVD CIGSe/Mo/glass p-n junction

Chalcopyrite absorber based photovoltaic technology (CIGSe) currently demonstrates the highest cell (>20%) and module efficiencies of all inorganic thin film technologies (12% for commercial modules and 13-14% for prototypes with typical areas of $0.35-0.70m^2$). In view of the efficiency-to-cost prospects of TFSCs, the present research work comprises the successive replacement of n- and p-type layer of CISe/CIGSe solar cells usually processed by in-vacuum Physical Vapor Deposition (PVD) techniques with layers processed by inexpensive chemical (CBD) and electrochemical (ECD) techniques. Low precursor costs, low processing variants, moderate process temperatures, large area deposition with perspectives of monolithic-module processing, relative fast deposition rates, and waste management through recycling are advantages of wet-processing techniques. In the frame of the present work, CBD ZnSe buffer- and ECD ZnO window-layers were deposited on PVD grown chalcopyrite absorbers. After optimization of layer thickness and dopant concentration, the respective p-n junctions of Au/In:ZnO/i-ZnO/ZnSe/CIGSe/Mo/glass exhibited I-V characteristics competing with mono-crystalline silicon(c-Si) I-V as demonstrated in Fig. 6. In addition, the research results of the present work demonstrate that novel, low cost electrodeposition approaches can yield by as few as possible process steps absorber layers with higher degree of crystallinity and sufficient homogeneity compared to those achieved with the one step in vacuum evaporation process.
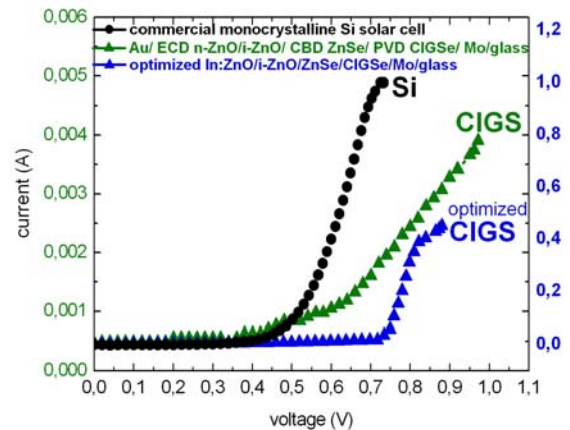

Figure 6: I-Vs of CIGSe and optimized CIGSe p-n junctions compared to (commercial) monocrystalline Si I-V.

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