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# Structural, optical, electrical properties, and strain/stress of electrochemically deposited highly doped ZnO layers and nanostructured ZnO antireflective coatings for cost-effective photovoltaic device technology

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ABSTRACT

High quality polycrystalline and nanostructured ZnO thin films were electrochemically deposited from aqueous solution of zinc nitrate ($Zn(NO_3)_2$) at negative electrochemical potential ($E_C = -0.6$ to $-1.4$ V) and moderate temperature (75–80 °C) on various substrates (Cu, Si, Mo/glass, ZnSe/Mo/glass, F:$SnO_2$/glass). Undoped (i-ZnO) films were grown free of strain on Cu and Mo/glass using intermediate lattice matched buffer (ZnSe). The i-ZnO films on Si exhibited high tensile in-plane stress of $\sigma = 4$ GPa. Growth rates depended on substrate orientation and electrochemical potential varying from $E_C = -1.1$ V for deposition on Si(100) to $E_C = -1.3$ V for optimum deposition on Si(111). Growth rates of undoped and doped (n-ZnO) films with Al and In dopant (Al:ZnO, In:ZnO) on Mo/glass depended on the solute dopant ($AlCl_3$, $InCl_3$) concentration (0.2 nm/s for i-ZnO, 0.7 nm/s for n-ZnO with n = 5 mM, 1.2 nm/s for n-ZnO with n = 9 mM). Hydrostatic compressive strains by incorporation of 0.4–12.0 at.% Al were in the range of $\varepsilon_h = -0.070$ to $-2.000$. The resistivity of metal-pin contacted n-ZnO/i-ZnO films (Me/Al:ZnO/i-ZnO/Mo/glass, Me/In:ZnO/i-ZnO/ZnSe/Mo/glass, Me: Au/Ni) was in the order $10^5$ Ω·cm. In the UV–VIS-NIR region (1.5–5.0 eV), the reflectivity of the films did not exceed 20% and the (optical) band gap of $E_g = 3.5$ eV indicated their high optical quality and material purity. The optical properties of electrochemically grown ZnO nanorod arrays (transparency: 70-80% at 1.5-3.0 eV and band-gap: 3.3–3.7 eV) were additionally analyzed by photoreflectance spectroscopy. By application of optical modulation techniques, both spectrally (4 meV at 300 K) and spatially (7 meV/cm) resolved gap energies were quantified and the role of nitric ($HNO_3$) and nitrate ($NH_4NO_3$) additives was extensively reinforced. Antireflective coatings (ARCs) of ZnO nanorods assembled in Cu(In,Ga)$Se_2$ thin film solar cells were found to quench the surface reflectivity by 5% at least. Integration of electrochemically processed transparent conductive ZnO films and ZnO ARCs in solar cell device technology is anticipated to provide key-solutions for cost effective energy harvesting.



## 1. Introduction

The present worldwide research activities on ZnO, its alloys, and nanostructures based on them, are driven by the vast potential of this material and its derivatives for optoelectronic, microelectronic, and photovoltaic applications. The renewed interest in ZnO applications for the photovoltaic is nowadays stimulated by the possibility of cost reduction in material processing and device development. Important aspects behind utilization of solar energy converters are, in fact, scale effects of mass production, technical advances, and cost reduction. Main objectives of the present research study are thus the controlled growth and material properties optimization of ZnO thin films and nanostructures by cost effective, moderate temperature, large area, fast rate electrochemical deposition (ECD) techniques, in general, and integration of ECD processed high quality transparent conductive zinc oxide layers and zinc oxide nanorod arrays, in particular, as window and antireflective coating of ECD chalcopyrite absorber solar cells towards inexpensive monolithic photovoltaic module assembly. The herein referred literature, though it includes several recent reviews of the ZnO research and articles on basic ZnO material properties, is specified in ECD processing of ZnO and its derivatives and focused on the overall application of inexpensive processes.

In chalcopyrite semiconductor based thin film solar cells (TFSCs), the photovoltaic junction is formed between the p-type chalcopyrite absorber, mostly $CuIn_{1-x}Ga_xSe_2$ (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). The devices consist of a metal-grid/n-ZnO/i-ZnO/CdS/CIGSe/Mo/glass layer sequence. Among various fabrication methods available for the absorber layer,

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electrochemical deposition (ECD) may be the most effective alternative to the expensive vacuum based techniques [1]. For high-efficiency CIGSe cells, the buffer layer is generally grown by chemical bath deposition (CBD) which is a low-cost, large-area wet chemical process. The preferred transparent conductive oxide (TCO) window of the cell consists of a bilayer of a thin (≤100 nm) ZnO film with lower and a ZnO film with essential higher lateral conductivity (to avoid ohmic losses) which both can be electrochemically deposited. By controlling the doping level of ZnO, its electrical properties can be sufficiently modified from insulator through n-type semiconductor to conductor while maintaining optical transparency that makes it useful for transparent electrodes in flat-panel displays and solar cells [2]. The TCO serves together with the metallic electron collector as the front contact of CIGSe cells. Basic research studies on the chemistry and physics of zinc oxide surfaces and adsorbates on zinc oxide surfaces inclusive theoretical calculations were published by Ch. Wöll in [3], F. Claeyssens in [4], and A. Janotti, C. G. Van de Walle in [5].

Another aspect driving the present research is the strong tendency of ZnO to self-organized growth in the form of nanorods [6]. A review of recent studies on ZnO nanostructures, their fabrication, device applications, and potential as an electron-acceptor material in hybrid solar cells is given in [7]. Vertical high quality ZnO nanorods (ZnO-NRs) grown by low cost electrochemical deposition (ECD) techniques are proven to be highly effective antireflective coatings (ARCs) for chalcopyrite based TFSCs [8]. ZnO single crystal nanorods have less deep defects than their respective thin film structures. They can be grown with high crystal quality by low-cost electrodeposition techniques and exhibit excellent material properties without the need of further annealing [9]. An ARC is an essential part of a solar cell and is employed to reduce reflection. Thickness and refractive index are key issues of an ARC. Most solar cells are provided with a conventional ARC made by a quarter wavelength thickness dielectric layer of $MgF_2$, SiN, $TiO_2$, or ZnS. It reduces the reflectivity in a certain wavelength range by destructive interference of waves reflected from the top and the bottom of the ARC [10]. The wavelength sensitivity can be further reduced by the use of a gradient refractive index layer [11], multiple layers [12], or trapping the incident light by structuring the surface of a solar cell [13]. Subwavelength structures confer an antireflective effect similar to the moth-eye effect [14]. Incident light cannot resolve the individual features on the surface leading to a gradual increase in effective refractive index from air into the patterned surface. This eliminates the discontinuity in refractive index at the interface and minimizes reflection. Studies show that subwavelength-structured arrays on the solar cell surface as an alternative to thin film ARCs exhibit low reflectivity over broad ranges of wavelength and angle of incidence [15] and can be more effective in reducing reflection.

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 [16]. 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 °C) and high temperature in vacuum processes (500–700 °C) [1,16]. The role of liquid-phase processing "*towards low-cost, environmentally friendly printed chalcopyrite and kesterite solar cells*" was convincingly defended by H. Azimi, Y. Hou, and Ch. J. Brabec [17] as they concluded that the most efficient solution processed chalcopyrite solar cells, published within the last 5 years, indicate a clear trend to better device efficiencies with a record published power conversion efficiency (PCE) of 15.2% based on pure solution deposition and a certified 17.1% printed CIGSe solar cell on flexible foil, announced by Nanosolar, bridging the performance gap to the highest efficiency vacuum-based devices with a PCE of 20.4%. For chalcopyrite ($Cu(In,Ga)Se_2$) and kesterite ($Cu_2ZnSn(S,Se)_4$) solar cells with absorbers processed by inkjet-printing a remarkable efficiency increase from 0.5% [18] to 5% at least for total area of 0.5 $cm^2$ [19] is currently reported. Nevertheless, ECD processing has already yielded PCE of this order on 25 $cm^2$ CISe cells [20].

Considering that ECD processes are highly depended on the conductivity of substrate and liquid phase electrolyte, in part 3.1 of Results and discussion, the structural and optical properties of intrinsic ZnO are investigated in dependence of the substrate conductivity (highly conductive copper (Cu) or semiconductive silicon (Si)). ECD i-ZnO is the *material of reference* for the ECD processed highly doped n-ZnO films and the nanostructured ZnO-NRs discussed in parts 3.2 and 3.3 of Results and discussion, respectively. Moreover, considering the applicability of highly doped ZnO als transparent conductive oxide (TCO) in solar cell device technology, principally, and in CIGSe and Si photovoltaics (PVs), primarily, ECD ZnSe buffer was used for i-ZnO deposition on Cu substrate and two different orientations of the Si surface, Si(100) and Si(111), were probed. Part 3.2 comprises then the main features of the ECD growth of highly doped ZnO, the structural characterization inclusive strain/stress analysis, and the electrical resistivity results of Al:ZnO/i-ZnO and In:ZnO/i-ZnO/ZnSe layered structures on Mo/glass substrates relevant for applications in CIGSe TFSCs. An essential part of the present work is devoted to strain/stress quantification, since elastic strain effects can induce material distortion and micro-fracture leading to device failure. Both mismatch and hydrostatic strain effects are successively and separately addressed within this work. Mismatch strains result from differences of the lattice constants and the thermal expansion coefficients of substrate and epilayer. Hydrostatic strains evolve in the crystal lattice from the incorporation of dopant (or impurity atoms) with different sizes as those of the host and may affect lattice-matched heterostructures as well. In part 3.3, both the structural and optical properties of ECD grown ZnO nanorods are thoroughly reinforced by means of Raman and Photoreflecance spectroscopy in view of fine adjustment of the ZnO-NR properties as highly efficient PV ARC.

Referred to actual research reports on electrochemically processed ZnO known from the literature, the present research study is hence indicated by its specific targets and the impact of its accomplishments, with the strain/stress quantification being of major importance for the development of cost effective efficient photovoltaic devices without barriers set by process or material incompatibilities.

For choosing the key investigation points, aspects of the international ZnO research have been taken into account and have among others driven the present research efforts as outlined in the following:

– Potentiostatic electrodeposition techniques were uniformly applied to process highly doped zinc oxide thin films on i-ZnO/Mo/glass and i-ZnO/ZnSe/Mo/glass substrates and nanostructured ZnO ARCs on i-ZnO/F:$SnO_2$/glass substrates with the aim to optimize and integrate both, n-ZnO and ZnO-NR ARCs, in solar cell device applications. The ZnO films were grown by ECD from $Zn(NO_3)_2$ solutions, alternately, in case of ZnO nanorod ARCs, from $Zn(NO_3)_2 + HNO_3$ and $Zn(NO_3)_2 + NH_4NO_3$, at moderate bath temperatures of maximum 80 °C, and negative electrochemical potential ($E_C$) depending on the end-product acquired (high quality very thin intrinsic or lightly doped ZnO films (i-ZnO), heavily doped ZnO films (n-ZnO), ZnO nanorod ARCs (ZnO-NRs)).

More positive electrodeposition potential favors the high quality growth of i-ZnO films, while annealing at moderate temperatures, between 300 and 400 °C, improves the (optical) quality assessment of the films, since it enhances and sharpens the excitonic (59.5 meV) by simultaneous decrease of the deep level emission, as has been observed in [21]. The energy band gap of electrodeposited films depends on $E_C$, which allows adjusting of the desired absorption edge within a 30 nm wide region in the UV as reported in [22]. Besides, band gap energies were found to decrease with the increase of bath temperature [23].