Compound semiconductor layers for optoelectronic and photovoltaic purposes

PhD Theses

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BUDAPEST, 2013

1. Motivation

Solar cells, as most members of renewable energy production, have recently been gaining a growing interest. Due to reports on global warming and energy needs the importance of developing new technologies in a cost-competitive way is the main motivation of thin film solar cells research.

As the visible light spectrum is between 1.6-3.4 eV, the active layer of a solar cell needs to have a band-gap not exceeding these values. A number of materials fulfil this requirement, and result in solar cells with various efficiencies and costs. The great advantage of thin film solar cells is that they have a low material requirement. The active layer of these devices has a thickness in the range of a few microns between two glass panes.

My theses focuses on thin films of two materials, both crucial for a number of photovoltaic applications: CIGS ($Cu(InGa)Se_2$), which is the absorber material of one of the most promising thin film solar cell family, and ZnO, which is the most commonly used transparent electrode material. As a wide band-gap semiconductor ZnO is also important for a number of optoelectronic applications as well.

CIGS materials are one of the most popular members of the thin film solar family as they combine cost efficiency with stability and a reasonably good efficiency. (20% for CIGS in laboratory scale) [1.1]. They can be prepared with a number of methods, but the processes that result in the best efficiency cells are extremely complex. Therefore there is a perspective of improving the fabrication of such solar cells significantly by the application of more economical and simpler deposition methods. The post selenization of copper, indium and gallium precursors is one of the most promising new directions for chalcopyrite fabrication. This technique is extremely simple and no expensive apparatus is needed, as the process is defined by the stoichiometry, and the parameters do not require precise tuning.

ZnO is a material with a direct band-gap of 3.37 eV, an exciton binding energy of 60 meV, and a very high radiation and thermal stability. It is piezoelectric, and can even be ferromagnetic if doped with transition metals. Unfortunately, up to now the lack of good quality single crystalline ZnO has hindered the advances concerning this material, but recently epitaxial growth on GaN has renewed interest in it. On the other hand transparent conductive oxides are crucial for a number of optoelectronic and electronic device applications as well, due to their very high exciton binding energy (60meV) [1.2]. A few examples are as TFTs, LEDs, field emitters, and flexible electronic devices. This application would require the growth of high quality epitaxial layers, preferably with a tuneable band gap and resistivity.

Another excellent application for ZnO would be as the buffer layer in CIGS solar cells. Usually CdS is used as this thin film between the active layer and the window electrode, but it is highly toxic and environmentally hazardous. It is also very impractical as its wet deposition interrupts the vacuum process [1.3]. However, sputtered ZnO does not grow with the required conformity on the CIGS film, therefore the use of a buffer layer is indispensable. Atomic layer deposited (ALD) ZnO would be a vacuum-compatible alternative, which even meets the requirements on

conformality, uniformity and reproducibility.

In the case of organic and hybrid solar cells it is crucial that the transparent conductive electrodes are always within a diffusion length from the location where the charges were generated. This requires high quality transparent conductive oxide materials grown in a number of high aspect ratio and surface/volume ratio structures on a nanometre scale. ALD ZnO is a perfect candidate to fulfil this immensely high requirement.

Goals

The aim of the present work is to examine the basic qualities and physical properties of thin films of two chosen materials: ZnO and $Cu(In,Ga)Se_2$.

- On the one hand to examine the basic physics of ALD deposited ZnO layers. The systematic investigation of Al doping and its effects on the conductivity is aimed, and the elaboration of novel structures from ALD ZnO for solar cell and opto-electronic purposes is targeted.
- On the other hand new, cheaper and simpler methods were tried to deposit the CIGS active material. One of the possibilities is the post-selenization method, that is, to anneal the CuInGa metals in Se atmosphere. This is an easily available method that enabled us to examine the processes and physical phenomena that take place during the selenization process of metallic precursors, and the required parameters of the absorber material.

Theses

1. I have shown that the ZnO films on Si and glass are polycrystalline, and have a preferred orientation as a function of the deposition temperature. In case of the 120°C substrate temperature, the (100) orientation is dominant, between 180°C and 210° a mixed orientation is typical, above this the (001) orientation dominates. The change of the orientation means that while at lower temperatures the c axis of the ZnO unit cell is parallel to the substrate; in the layers deposited at higher temperatures the c axis is perpendicular to the substrate surface. The Al doping reduces the crystallinity of the layers, decreases the grain size and induces strains in the film. The best crystallinity in doped layers is resulted by a 2at% Al doping.

   Thesis 1. was published in:

   T1: Structure and morphology of aluminium doped Zinc-oxide layers prepared by atomic layer deposition: Zs. Baji, Z. Lábadi, Z. E. Horváth, I. Bársony, Thin Solid Films 520 (2012), 4703. IF: 1.89

2. I have studied the Al doping of ALD ZnO using alternative precursor pulse methods. I have shown that the incorporation of Al occurs mostly in the form of Al_2O_3. The doping efficiency depends on the deposition temperature and has its optimum at 210°C and 2 at% Al concentration. The carrier concentration has a maximum of $2.5*10^{20}/cm^3$ in this range while the mobility monotonously decreases with the doping. The conductivity is not grain boundary dominated.
I have deposited highly conductive epitaxial ZnO layers on GaN substrates by atomic layer deposition for the first time. The layers grown above 270°C are epitaxial and exhibit low resistivity in the order of magnitude of $10^{-4}\Omega cm$. Lower temperature epitaxial growth is also possible by the introduction of an epitaxial buffer layer. I have shown that the source of this high conductivity is the Ga doping from the substrate. Additional Al doping deteriorates the quality of the epitaxy.

Thesis 2. was published in:
T2: Temperature dependendent in situ doping of ALD ZnO: Zs. Baji, Z. Labadi, Z.E. Horvath, M. Fried, B. Szentpali, I. Barsony, JTAC 105 (1) 93-99 (2011) IF: 1.75
Independent citations: 4
T3: Al doped ALD ZnO for CIGS buffer layer, Zs. Baji , Z. Lábadi , M. Fried K. Vad J. Toth and I. Bársony, Proc. EUPVSEC, 2011, 2992 - 2997 ISBN: 3-936338-27-2 DOI: 10.4229/26thEUPVSEC2011-3DV.2.26
T4: Microscopy of ZnO layers deposited by ALD, B. Pécz, Zs. Baji, Z. Lábadi, and A. Kovacs, Thin Solid Films, accepted (2013) IF: 1.89

3. I have shown that ALD ZnO exhibits a layer by layer growth on sapphire and GaN substrates, and an island-like growth on Si. The reason for the latter is a seed formation issue on the SiOx surface which can be overcome by applying a 10-100 times longer first deposition cycle.
I concluded that besides the surface chemical reactions the temperature dependence of the growth rate of ALD ZnO on Si is caused by the orientation. At higher temperatures the steric hindrance of the neighbouring adsorbate molecules results in their reconfiguration in the next closest packing structure.
I have also shown that the difference of the growth rates on different substrates is a result of the different morphologies of the grown layers. The layers grown on Si have a higher roughness, therefore a larger specific surface, which yields a higher rate of adsorption.

Thesis 3. was published in:
T5: Nucleation and Growth Modes of ALD ZnO, Zs. Baji, Zoltán Lábadi, Z. E. Horváth, G. Molnár, J. Volk, I. Bársony, P. Barna, Cryst. Growth Des., 12. (2012) 5615 IF: 4.7

4. I have developed a $Cu(InGa)Se_2$ deposition method using a flash-like evaporation of Cu In and Ga followed by post-selenization. The resulting layers are homogenous CIGS films with the required composition and crystalline structure. I found that the rough

morphology of the precursor layers has no negative effect on the structure and morphology of the final CIGS layers as the Ga concentration was found to be uniform throughout the whole thickness.
In the case of the consecutively evaporated precursor metals I found that the morphology of the deposited metals has a definitive effect on the resulting CIGS structure. Therefore I determined the optimal order of the precursor metals as: In followed by Ga, then by Cu. The reason for this is that the Cu sputtered in the final step ensures the mixing of the precursors due to the Ga diffusion. On the other hand the Ga evaporated before the In results in a phase separation of the CIS and CIGS materials.
The selenization must be performed as an annealing in Se vapour, as the evaporation of Se and a subsequent annealing is not sufficient for all the reactions that would result in a homogeneous CIGS layer to take place.

Thesis 4. was published in:
T6: Post-selenization of stacked precursor layers for CIGS, Zs. Baji, Z. Lábadi, Gy. Molnár, B. Pécz, A. L. Tóth, J. Tóth, A. Csik, and I. Bársony, Vacuum, 92. (2013) 44 IF: 1.2
Partly related to thesis 4.:
T7: Formation of Nanoparticles by Ion Beam Irradiation of Thin Films, Zs. Baji, A. Szanyo, Gy. Molnár, A. L. Tóth, G. Pető, K. Frey,E. Kotai, and G. Kaptay, Journal of Nanoscience and Nanotechnology 12, (2012)1. IF: 1.4

Further publications not closely related to the subject of this work:

1. Investigations into the Impact of the Template Layer on ZnO Nanowire Arrays Made Using Low Temperature Wet Chemical Growth: Erdelyi R, Nagata T, Rogers DJ, Teherani FH, Horvath ZE, Labadi Z, Baji Zs, Wakayama Y, Volk J CRYST GROWTH DES 11: (6)2515-2519 (2011) IF:4.7
   Independent citations: 5
2. Thickness and annealing dependent morphology changes of iron silicide nanostructures on Si(001) G. Molnár, L. Dózsa, Z. Vértesy, Zs. Baji, G. Pető, (2012) DOI:10.1002/pssc.201100662, Copyright (c) 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
3. Characterization of ZnO structures by optical and X-ray methods, P. Petrik, B. Pollakowski, S. Zakel, T. Gumprecht, B. Beckho, M. Lemberger, Z. Labadi, Zs. Baji, M. Jank, A. Nutsch, Thin Solid films, http://dx.doi.org/10.1016/j.apsusc.2012.12.035 (2013) IF 1.89