LABORATOIRE CHARLES COULOMB MONTPELLIER

Dr Olivier BRIOT
Directeur de Recherche CNRS
Equipe « Matériaux, Semiconducteurs et Capteurs »
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Object : Report on the manuscript written by M. Tomasz Drobiazg in view of obtaining the Ph.D in physics at the Warsaw University of Technology, Poland.

The manuscript written by M. Tomasz DROBIAZG is entitled "Impact of $Cu(InGa)Se_2$ thin film growth process on the electrical metastabilities of related solar cells", in view of presenting his work to obtain the Ph.D degree, from the Faculty of Physics, at the University of Warsaw (WUT), Poland.

The manuscript is divided in 9 chapters with two appendices. I was at first surprised by the large number of chapters, several of them being 1 to 4 pages in length, while chapter 7 represents half of the manuscript. Although I would have liked to see a more balanced structure, the manuscript is well written, pleasing to read and highly interesting.

In chapter 1, M. Drobiazg introduces the concepts of photovoltaic (PV) energy production, and introduces in chapter 2 the aim of his Ph.D work.

Chapter 3 sets the context of the subject by summarizing its history, detailing the properties of the base material, which is the quaternary alloy $CuIn_{1-x}Ga_xSe_2$ (CIGS), and explaining the structure of a CIGS solar cell device. Then Tomasz Drobiazg presents in details the technological steps involved in the growth of all the layers that constitute a full cell. At this point, the reader can understand that he has fabricated himself the samples involved in his work and has gained a lot of know-how on this part. This is, in my opinion, a strong point in his work, that he had the opportunity, and made the necessary efforts to learn sample growth techniques. This allows him to get a deeper understanding of the physical system he is working on. From there, he explains the basic physics of the CIGS solar cell (equivalent model, recombination paths, defects and metastabilities), with appropriate references to the literature and listing the main equations that will be used to analyze the experimental data later on.

Chapter 4 could have been easily merged with chapter 3, since it continues with the presentation of the theoretical and experimental tools involved in the thesis work. Of particular importance, clear explanations are given here on the steps used in the preparation of the different metastable states examined in this work : "relaxed", "reversed biased" and "white light soaked". Here, it would have been interesting to present the light spectrum of the white LED used in several measurements, in order to understand precisely in which way it differs from the STC (standard test conditions with AM1.5 solar simulator). Numerous structural characterization methods, like Electron microscopy, X-ray diffraction, EDX, SIMS, were also used and this indicates that Tomasz Drobiazg had to learn and master many techniques, contributing to give him a broad spectrum of competences, as a physicist.

In chapter 5, he introduces the statistical analysis he performed on the electrical data (current – voltage), using both the standard equivalent model and an improved model which adds a new, non-linear, shunting term and introducing in both the influence of tunneling effects. He describes the statistical techniques used to validate the fitting parameters involved in the abovementioned models, which clearly involve intensive computation (Monte Carlo simulations were performed to obtain the uncertainties ...). In my opinion, this is a real novelty and added value in the present analysis, as it brings more confidence on the selection of the appropriate recombination model, for each set of data.

Chapter 6 is dedicated to modeling the shape of the x-ray diffraction peak, in order to analyze in depth the spatial compositional profile. This is of high importance since this compositional profile translates into a bandgap profile, which has strong effects on the absorption of photons and collection of charge carriers. The model used here is elegant in its simplicity; however it consists in linearly summing the contributions of each composition to the whole intensity profile, thus ignoring possible interferences effects (the base of diffraction) and the fact that the impinging intensity at a given depth may be reduced by the strong diffraction occurring in the part of the layer immediately above. Also, each diffraction contribution may have its own width due to domain sizes along the growth axis (different from grains sizes) for example, ... Although a discussion of these effects would have been nice, the success of the model established by Tomasz Drobiazg is clear from the way it fits the experimental data. The work done here is characteristic of the approach of Tomasz, in trying to have a model at hand to go beyond the pure experimental approach and obtain a deeper insight on the phenomena at work.

Finally, with the "large" chapter 7, we are at the core of the Ph. D work. It is composed of 3 subparts that correspond to different sample sets :

In part 7.1, the "A" sample set is analyzed. It has been designed to investigate the effects of both the transition speed, when going from the cu-poor to cu-rich phase in the growth, and the whole second step duration (copper addition) on the sample properties and metastable defects occurrence. A clear "workplan" is followed, that is : sample design, structural characterization, photovoltaic characterization, fill-factor and open circuit voltage analysis, electrical transport (I-V (T)) analysis and then capacitance measurements. I am really admiring the amount of work realized in doing so, since the volume of experimental data, as well as the amount of analysis work, is huge. M. Drobiazg is led to the following conclusion : a slow transition from copper poor to copper rich phase is clearly beneficial - it improves the crystalline quality by producing larger grains, limiting the importance of secondary barriers, lowering the amount of tunneling in the space charge recombination and lowering the concentration of metastable defects.

In part 7.2, another set of sample ("B") is designed and grown to investigate the influence of band gap and band gap gradients. The band gap gradients are "artificially" created in three samples, and these samples are compared to 3 samples without gradient, but of varying bandgap values. The same workplan as in part 7.1 is followed. I was surprised by the relatively high values of the PV parameters (Icc, Voc, FF, efficiency) obtained in these samples, grown by a simple one step process. These samples led M. Drobiazg to interesting conclusions : on the structural aspects, the texture of the samples is different with less (112) orientation both for non graded and graded samples. The grain structure is very columnar, mostly independent of the bandgap (Ga concentration). Collection is improved in graded samples; in parallel recombination rate is increased by the gradient - I wonder if the localization at the notch could cause enhanced radiative recombination - and both tunneling and metastabilities show a marked correlation with the bandgap value.

Last, part 7.3 is based on an even larger set "C" of samples, aimed at probing the influence of sodium and bandgap grading, in both recrystallized (3 step process) or non-recrystallized samples. Despite the larger number of samples, the exact same characterization and analysis procedure as in the previous two cases is followed. We now have 8 types of samples, with 3 metastable configurations investigated, at various temperatures. This result in a large and complex amount of data, summarized in (sometimes) complex graphs that require the full concentration of the reader - However, this reflects the working power of the candidate and leads to rich conclusions : the preferential orientation, as determined by diffraction peaks, is controlled by two factors : the amount of sodium and the recrystallization, the latter being the main factor. The presence of sodium has an impact on the diffusivity of gallium, and this changes the final composition profile in the case of recrystallized samples. The incorporation of sodium has an already well known impact on the PV parameters, but original results are obtained here regarding the impact on sodium on the secondary barriers and metastabilities - this is well summarized, despite its complexity in the conclusions of part 7.3.

Finally, chapter 8 is a summary and comparison of the three sets of samples. A Meyer-Neldel plot of all detected defects allows us to realize that two types of defects, that had already been identified in a previous work, are present here.

To summarize, Tomasz Drobiazg has realized a huge amount of work, both in the experimental part and at analyzing the physics involved. I have particularly appreciated his rigorous approach, by trying to make a detailed statistical evaluation of the data, and in never "over-analyzing" the data to try to extrapolate too far. The results are original, useful and interesting. He has clearly demonstrated that he acquired a lot of competences during his Ph.D, from material growth, device

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technology, advanced characterization, applied to structural and electronic properties. The manuscript is well written and I had a lot of pleasure to work on it. I have the feeling that Tomasz Drobiazg is now an accomplished physicist and in view of the preceding remarks, I have no hesitation to strongly recommend to proceed to the thesis defense, in view, for Tomasz Drobiazg, of obtaining the doctor's degree from the Warsaw University of Technology.

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Dr. Olivier BRIOT

Laboratoire Charles Coulomb, L2C, UMR5221 CNRS

Université de Montpellier, France