Spectroscopic Ellipsometry for CIGS ($CuIn_{1-x}Ga_xSe_2$) thin films characterization

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Abstract
CIGS is one of the most efficient solar cell absorbers and used in a number of solar cell structures. Consequently, non-destructive characterisation of the material is very important. Spectroscopic ellipsometry is a technique perfectly adapted for such task: it is fast, non-contact and can be realized in a real fab environment. The challenge for such characterisation is the accurate determination of the optical functions of CIGS and this is essentially related to the large surface roughness always present, whatever the deposition method. This application note presents a convenient approach to the ellipsometric characterisation of CIGS, using an optimised surface etch method tailored to minimize the errors in optical properties determination induced by surface roughness.

Key words
CIGS, optical properties, surface preparation, spectroscopic ellipsometry

Introduction

Copper indium gallium selenide ($CuIn_{1-x}Ga_xSe_2$ or CIGS) alloy is a direct bandgap semiconductor which is a particularly efficient solar energy converter in a thin film configuration.
CIGS films can be manufactured by several different methods. The most common vacuum-based process is to co-evaporate or co-sputter copper, gallium, and indium onto a substrate at room temperature, then to anneal the resulting film with a selenide vapor to form the final CIGS structure. An alternative process is to co-evaporate copper, gallium, indium and selenium onto a heated substrate. As a consequence, these types of deposition produce a roughness layer at the surface, preventing efficient optical characterization.

A wet chemical etching procedure [1,2,3] was applied to the samples to significantly decrease their roughness and to leave an homogenous and flat surface, allowing easier optical characterization of the CIGS layer by spectroscopic ellipsometry.

The etching rate is time linear and is very reproducible, it is possible to stop the etching procedure at a given thickness in the range between several µm and 200 nm. This etching procedure is based on $HBr:Br_2:H_2O$ chemical formulation and also gives rise to a very reproducible final surface chemistry with an ultra thin (Se°) capping of the flattened surface. Oxide formation is therefore eliminated, yielding optimal samples for optical characterization. Finally KCN treatment is able to release the ultrathin Selenium capping which allows an additional condition for accurate optical characterization.

Experiment

Six CIGS samples, one without and five with different wet etching times have been measured using the UVISEL 2, the new Phase Modulated Spectroscopic Ellipsometer.

Figure 1: UVISEL 2

The graphics after display the ellipsometric spectra of these six samples. These experimental data show the different response of ellipsometer depending whether the sample has been wet etched or not. This difference is enhanced from 1.5 eV, over the absorption spectral range of the coating.

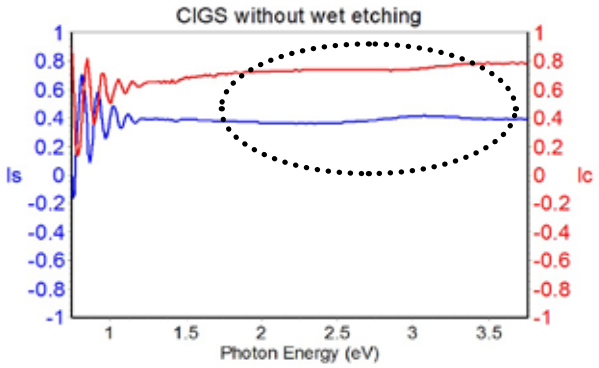


Figure 2: CIGS without wet etching

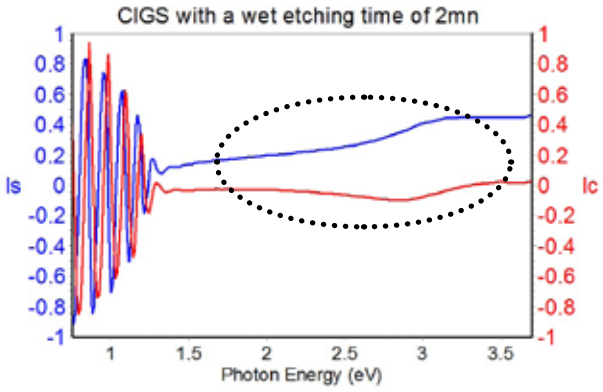


Figure 3: CIGS with a wet etching time of 2 min

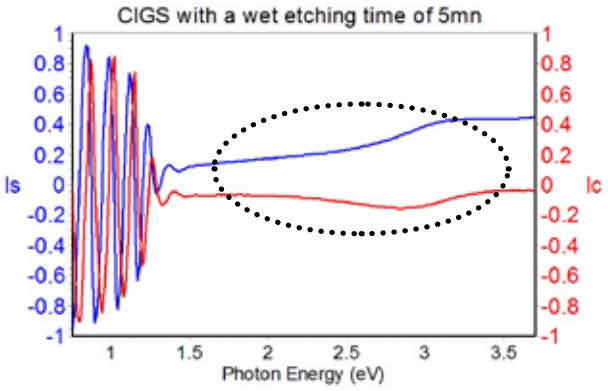


Figure 4: CIGS with a wet etching time of 5 min

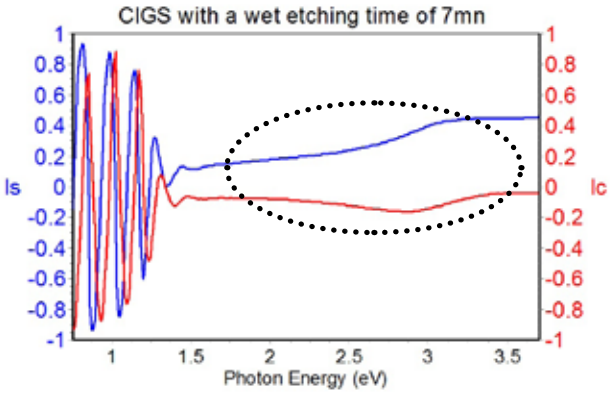


Figure 5: CIGS with a wet etching time of 7 min

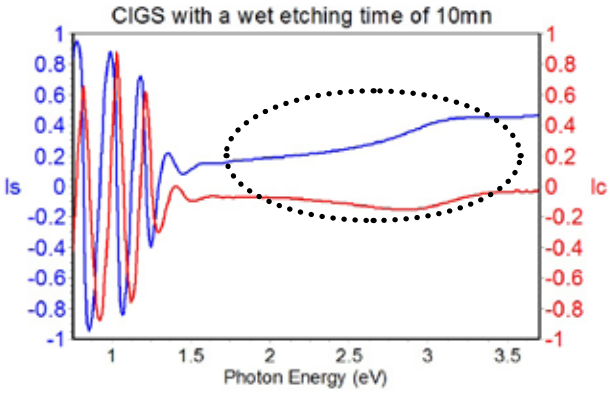


Figure 6: CIGS with a wet etching time of 10 min

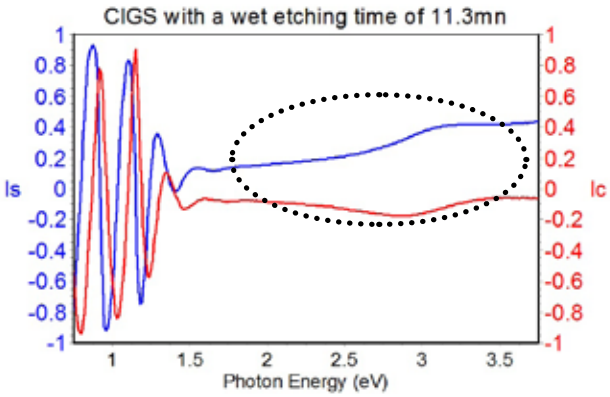


Figure 7: CIGS with a wet etching time of 10 min

Thus, from an etching time of two minutes, we can see that the ellipsometric response is stabilized, showing that the roughness has been considerably reduced.

Moreover, the profile from a pulsed RF GD-OES profilometer (HORIBA instrument) and a XPS instrument confirmed the homogeneity of the alloy and the minimized surface roughness.

Results

The ellipsometric data was analysed using a two-layers model. Despite the wet chemical etching, the samples still exhibit a thin rough overlayer on top of the GICS layer.

A “Bound Multimodel” was applied using four data sets with etching times of 5, 7, 10 and 11.3 minutes.

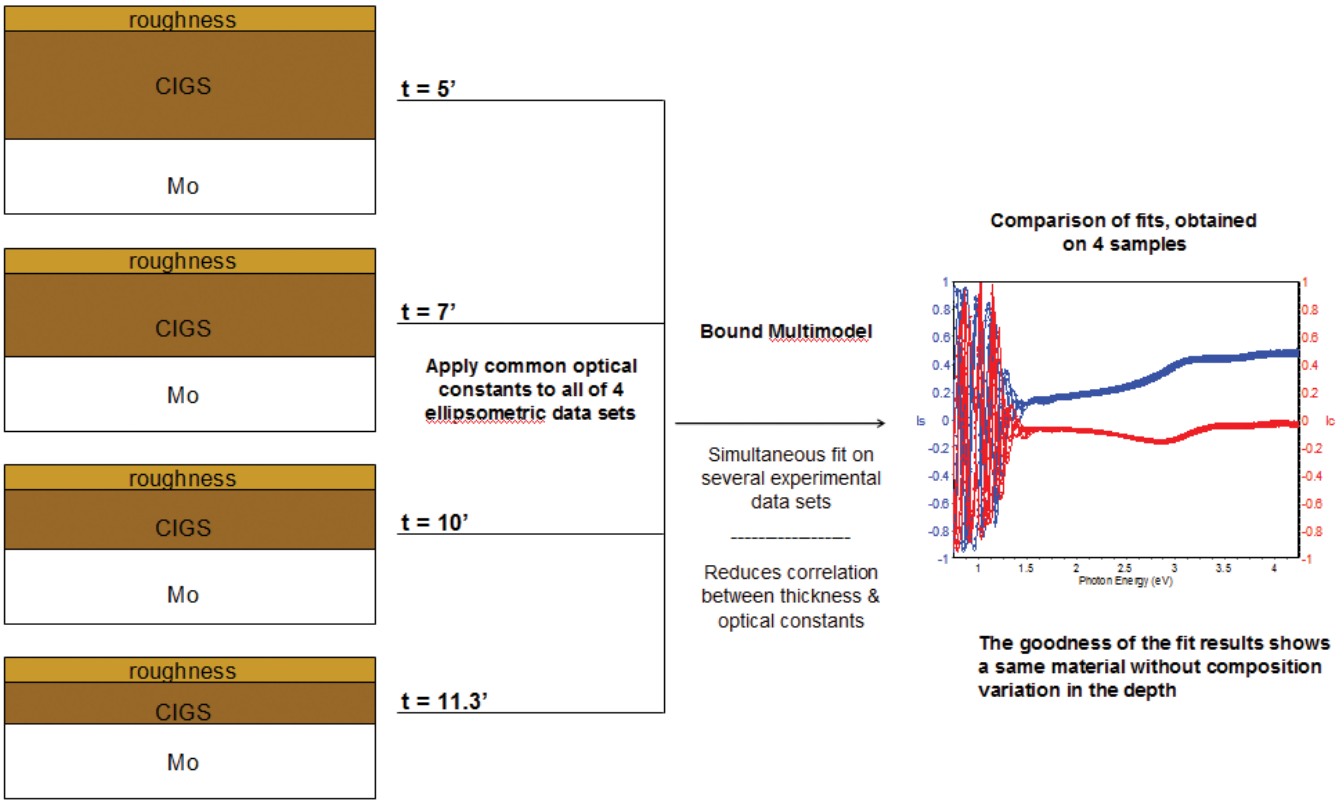
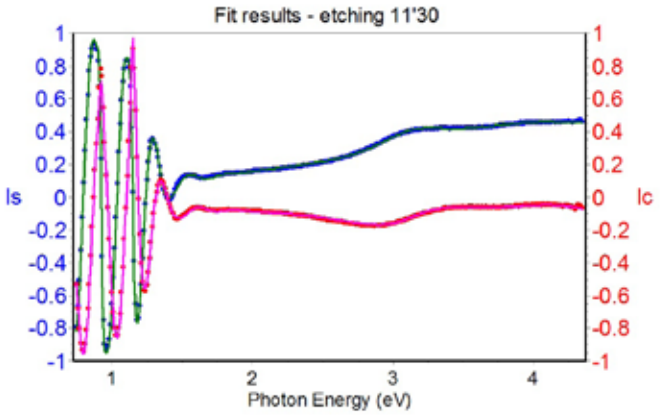


Figure 8: Multi-model results

The CIGS optical constants were determined using a Cody-Lorentz dispersion formula to model the small absorption below and above the band gap. And we associated 3 Lorentz oscillators to model absorption peaks up to 4.2 eV. The following graph shows the excellent agreement of the fit for the sample 11'30 and the thicknesses are summarized in the following table.



.... Experimental data — Fit data

Figure 9: Fit results - etching time 11'30

	CIGS layer thickness (nm)	Roughness layer (nm)	Expected thickness (nm)
5'	1442	2.7	1550
7'	1212.9	2.9	1200
10'	917.4	3.4	720
11.30'	581.1	1.6	450

The expected thicknesses are calculated from a global surface (several cm^2) of sample and this can be affected by the sample edge. This is most likely to have occurred for the 11.30' sample and this would explain the difference between the measured and expected thickness in this case.

The CIGS optical constants are displayed in the following figure. The parameters of the Cody Lorentz formula allow the CIGS optical band gap energy to be deduced. It is related to the Gallium composition. The band gap value is Eg = 1,16 eV, and E1 = 3.06eV, E2=3.92eV.

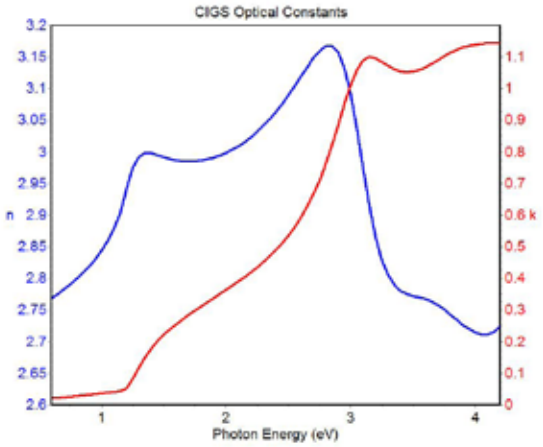


Figure 10: CiGS optical constants

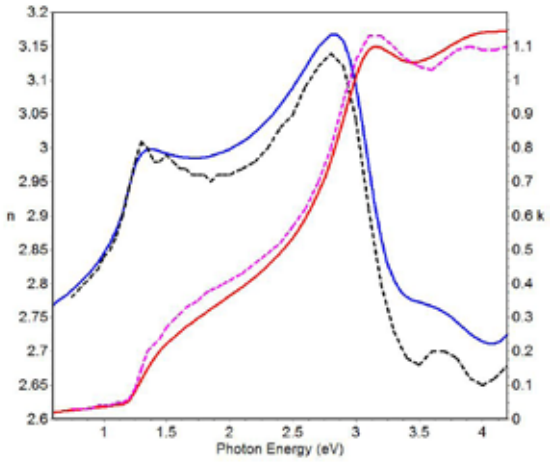


Figure 11: Comparison of our CIGS optical constants with CIGS data from Paulson [4]

Conclusions

In this work we have demonstrated the use of an HORIBA Scientific spectroscopic ellipsometer for non destructive characterization of CIGS. Thickness, optical constants and bandgap were determined by ellipsometry. A wet chemical etching procedure was necessary to remove the thick surface roughness layer as this caused partial specular reflection and would have required complex roughness film modelling.

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