

In-situ measurement of nanoscale thin film thickness for next-generation photovoltaics

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Abstract

This project addresses two key objectives in thin film research: improving thickness control during deposition and investigating CuAlFeS₂ as a potential intermediate band semiconductor for photovoltaic applications. Real-time thickness monitoring was implemented using a Quartz Crystal Microbalance (QCM) integrated into a Nano-PVD magnetron sputtering system. To calibrate the QCM, the tooling factor was experimentally determined by comparing QCM-reported values to actual film thicknesses measured via optical profilometry across three titanium films. A tooling factor of 66.7% was obtained for one magnetron gun, consistent with expected geometric disparities between the sensor and substrate. In the second phase, CuAlFeS₂ thin films with varying aluminium content were fabricated via co-sputtering from CuFeS₂ and Al targets. Energy-Dispersive X-ray Spectroscopy (EDS) confirmed partial incorporation of Cu, Al, and S; however, Fe was not detected, likely due to low sputtering efficiency and preferential ejection of other species. These findings highlight the limitations of RF sputtering for complex quaternary compounds under non-reactive conditions. This work provides a foundation for future optimisation of real-time thickness control and compositionally tuned synthesis of CuAlFeS₂ for photovoltaic applications.

Keywords: Quartz Crystal Microbalance (QCM), Tooling Factor, Magnetron Sputtering, Thin Film, CuAlFeS₂, Chalcopyrite, Photovoltaics.

Introduction

This project was funded by the Undergraduate Research Opportunity Scheme (UROS) (Lincoln, 2015) – a competitive bursary scheme that allows collaborative research

between students and academics. The scheme follows the 'student as producer' model; as such, the undergraduate takes on the roles of researcher and author (Strudwick, 2021). This project consisted of two parts: the first sought to develop the capability to measure the thickness of thin films during deposition, and the second to fabricate and investigate CuAlFeS_2 samples as a potential intermediate band semiconductor for the absorbing layer material in next-generation photovoltaics (Dickens *et al.*, 2022).

Project Background

Thin films are at the forefront of many emerging technologies, including batteries, corrosion-resistant coatings, and solar cells. The thickness of a thin film plays an important role in determining its physical and functional properties (Sakthinathan *et al.*, 2025). At the University of Lincoln, thin films are fabricated using magnetron sputtering, a physical vapour deposition (PVD) technique; however, the current system only allows for post-deposition thickness measurement, which limits process control and reduces research output.

A quartz crystal microbalance (QCM) placed inside the Nano-PVD deposition chamber can be used to monitor film thickness in real time during deposition. However, the thickness measurement obtained corresponds to the film deposited on the quartz crystal sensor, not on the actual working substrate. Due to the geometry of the QCM relative to the substrate, the thickness of the film deposited on the substrate often differs from that on the QCM (Ohring, 2001). This discrepancy is accounted for by a correction factor known as the tooling factor (Hardy, 2013). Hence, the first aim of this project will be to experimentally determine this factor for the existing sputtering system.

As mentioned, one of the applications of thin films is in next-generation photovoltaics (Solar Cells). CuAlFeS_2 is a promising intermediate band semiconductor, and computational studies have suggested that the substitution of Fe with Al can enhance photothermal efficiency compared to CuFeS_2 , potentially improving solar energy conversion (Dickens *et al.*, 2022). Consequently, the second objective of this study is to fabricate CuAlFeS_2 thin films with varying aluminium concentrations using co-deposition via nano-PVD. Then to experimentally verify the computational predictions made by Dickens *et al.* (2022) using optical spectrometry, specifically by analysing the films' absorption spectra and estimating their optical band gaps.

Literature Review

As a film is deposited, material accumulates on both the QCM crystal and the working substrate. Quartz is a piezoelectric material that vibrates at a precise resonant frequency, f_0 . The added mass on the QCM causes a measurable shift in its resonant

frequency (Ohring, 2001). This normalised frequency change, Δf , can be correlated to the change in mass, Δm , and thus film thickness, using the Sauerbrey equation:

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q\mu_q}}\Delta m \quad (1)$$

where A is the piezoelectrically active crystal area, ρ_q is the density of the quartz and μ_q is the shear modulus of the quartz, for AT-cut crystal.

It is estimated that the world will require 30 TW of power by 2050 to sustain economic growth. Solar energy is a leading candidate to meet this demand while reducing dependence on fossil fuels; however, despite silicon-based solar cells dominating the market, they remain limited by high production costs, rigid substrates, and energy-intensive fabrication (Asim, 2012). These drawbacks have prompted interest in next-generation photovoltaic materials.

Chalcopyrite, one of the most earth-abundant copper ores, has been studied for millennia and continues to attract interest (Dickens *et al.*, 2022). Multiple studies report an optical resonance around 500 nm in CuFeS₂ nanomaterials, attributed to the presence of an intermediate band, making the material a promising semiconductor for photovoltaics due to its photothermal conversion efficiency and elemental abundance (Chen *et al.*, 2013; Ghosh *et al.*, 2016). Current Cu(In,Ga)Se₂ thin-film solar cells have achieved power conversion efficiencies exceeding 22% and offer long-term stability and reproducibility (Naveena *et al.*, 2020). However, the key elements in these devices are rare and expensive. In contrast, CuAlFeS₂ is based on more abundant and non-toxic materials, making it a promising low-cost alternative (Naveena *et al.*, 2020; Dickens *et al.*, 2022).

Methodology

The first objective of this project was to determine the tooling factor of the QCM integrated into the Nano-PVD system. This required establishing the discrepancy between the film thickness indicated by the QCM and system software, and the actual film thickness deposited on the working substrate. It was established that coatings needed to be in the micron range to produce reliable step-height measurements with the optical profilometer. Three Ti films were deposited with thicknesses of 1 µm, 2 µm, and 4 µm, as indicated by the QCM software. All films were deposited using DC magnetron sputtering. To enable step-height measurement, each substrate was partially masked using metal clips placed at the centre, creating a defined step edge. After deposition, ten profilometer measurements were taken across the step edge for each sample to calculate the actual film thickness and determine the tooling factor.

The second objective was to determine the optical band gap of CuAlFeS₂ films with varying Al concentrations. A CuFeS₂ ceramic target and a metallic Al target were used,

as a pure Fe target would interfere with the magnetic field, preventing plasma ignition. In magnetron sputtering, a target is the source material from which atoms are ejected and deposited onto a substrate to form a thin film. The Nano-PVD system enabled co-deposition, with RF sputtering used for the CuFeS₂ target and DC sputtering for the Al target. Films were deposited onto ITO-coated glass substrates.

Although the QCM was initially intended to monitor deposition rates on the working substrate and estimate the CuFeS₂-to-Al ratio of the deposited films, it became non-functional during this phase. Instead, we exploited the fact that DC sputtering has a significantly higher deposition rate than RF sputtering. The ceramic target was operated at 50 W, the highest stable power without compromising plasma stability or damaging the target. Al was deposited at low powers of 1 W, 2 W, 3 W, and 4W to control Al incorporation.

To assess the elemental ratios of Al to CuFeS₂ in the films, energy-dispersive X-ray spectroscopy (EDS) was used. Because the films were too thin for reliable analysis at the standard 10 keV accelerating voltage typically required to excite secondary peaks, a reduced voltage of 5 keV was employed for all measurements.

Results

To determine the tooling factor, the mean film thickness was calculated for each of the three Ti samples based on ten measurements taken across the substrate surface. The tooling factor was then computed using:

$$\text{Tooling Factor} = \frac{T_s}{T_Q} \times 100 \quad (2)$$

where T_s was the average measured thickness on the substrate and T_Q was the thickness reported by the QCM. The final mean tooling factor of 66.7% was consistent with expectations, since the QCM sensor was positioned significantly closer to the sputtering targets than the substrate, resulting in a higher material flux and a thicker film on the QCM. Figure 1 shows one representative set of thickness measurements, with dashed lines indicating the QCM-reported thickness. The deviation illustrates the need for a tooling factor correction.

This value was determined for only one of the three magnetron guns. The QCM ceased functioning before equivalent measurements could be obtained for the other two guns. Since the QCM was not centrally positioned relative to the three targets, geometric asymmetries were expected to produce different tooling factors for each gun.

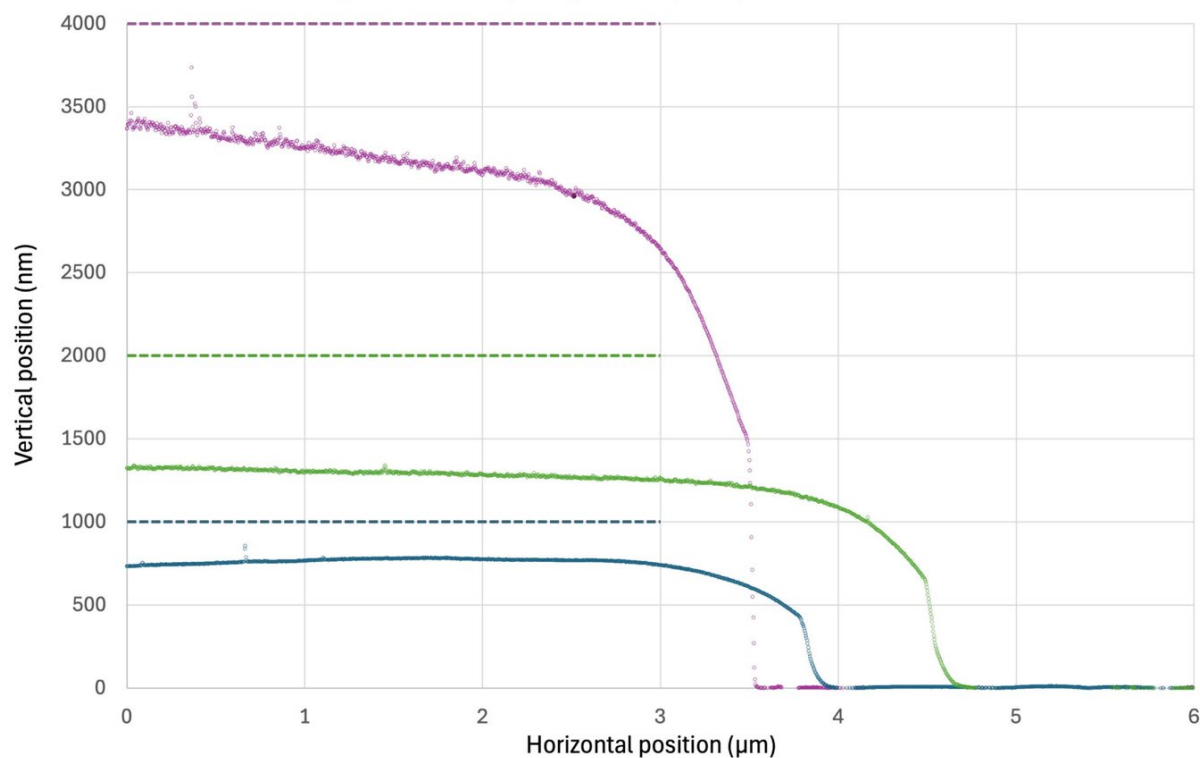


Figure 1: Surface profiles of 1 μm , 2 μm , and 3 μm Ti films, with dashed lines showing QCM-reported thicknesses.

To determine the elemental composition of the four CuAlFeS_2 samples, EDS was employed. The emission spectra obtained for each sample are shown in Figure 2, corresponding to increasing DC sputtering powers applied to the Al target.

Elemental analysis revealed the presence of Si, O, and In, which originated from the underlying ITO-coated glass substrate, along with Mg and Na contamination.

Cu and S were present in all samples except DC1. Since all depositions were performed for the same duration with only DC magnetron power varied, film thickness was expected to increase with power. The absence of Cu and S in DC1 was likely due to the film being too thin to produce measurable signals.

Although S was detected in DC2–DC4, it appeared only in small amounts. This was expected, as S sputters inefficiently due to its volatility, low yield, and tendency to re-evaporate. These limitations are worsened in systems without a reactive S atmosphere, such as H_2S gas or RF-cracked S plasma, which are often used in reactive sputtering (Motai *et al.*, 2025).

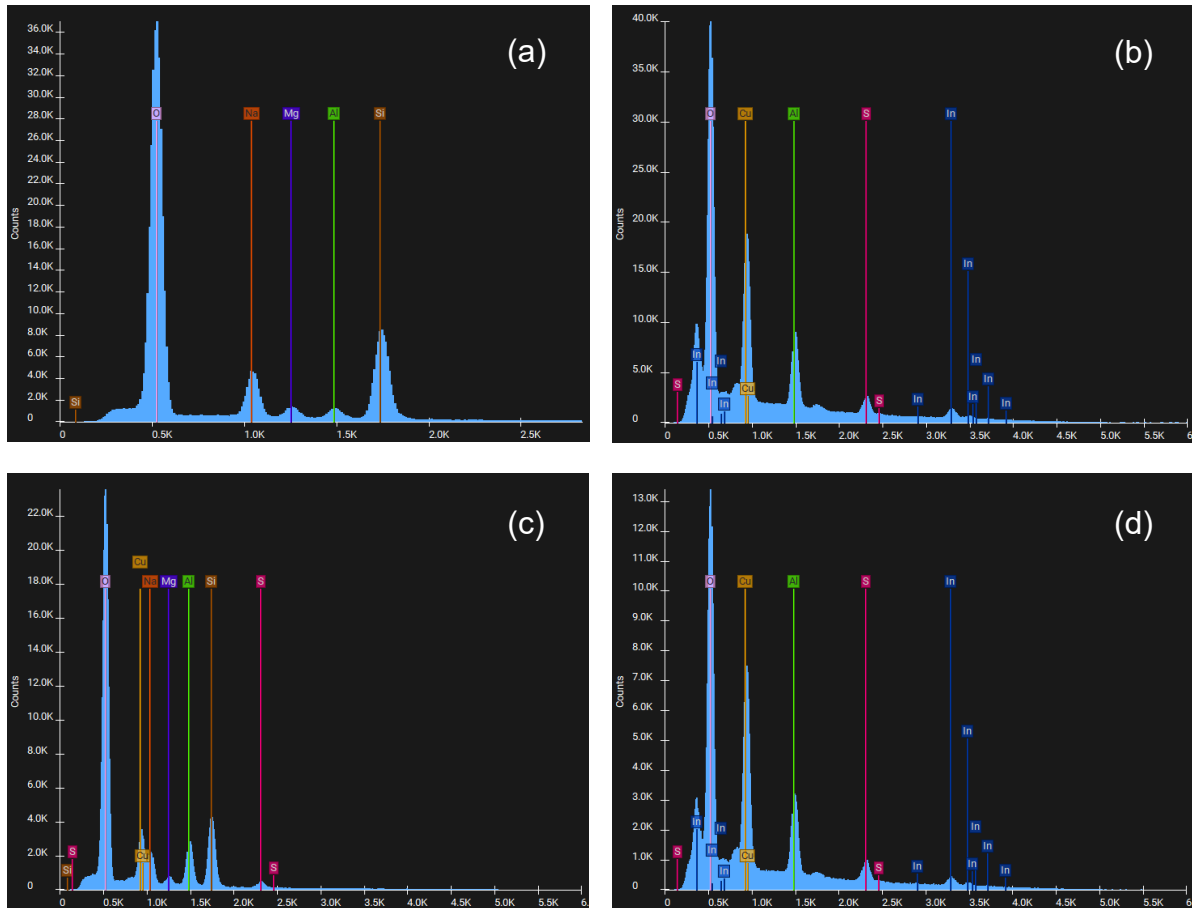


Figure 2: Emission Spectra from EDS for the 4 substrates where DC sputtering power was increased: (a) 1 W, (b) 2 W, (c) 3 W, and (d) 4 W.

Cu was detected in DC2, DC3, and DC4, although DC3 showed a notably weaker intensity. Despite increasing the DC power to the Al target, there was no clear trend in Al peak intensity.

No Fe was detected in any of the samples. This may have been due to preferential sputtering of Cu and S from the compound target, along with Fe's low sputtering yield under these conditions. Additionally, Fe atoms may be more tightly bound within the ceramic matrix, making ejection inefficient during RF sputtering (Mattox, 2010; Wasa et al, 2012). To overcome these issues, alternative methods such as chemical spray pyrolysis have been used to successfully synthesise CuAlFeS_2 films (Naveena *et al.*, 2020).

UROS Experience

Conducting this project has given me valuable insight into the realities of scientific research, from writing a funding proposal to managing experimental setbacks and

completing the final report. I gained hands-on experience with advanced equipment not typically used during undergraduate studies, such as the Energy Dispersive X-ray Spectroscopy (EDS) system and the Nano-PVD Magnetron Sputtering Machine, which I learned to operate and troubleshoot. When key equipment became unavailable, I had to adapt and revise my experimental approach, improving my problem-solving and experimental design skills.

This project confirmed my ambition to pursue a career in experimental physics. I am especially grateful to my supervisor, Dr Matt Booth, for his support and encouragement throughout the project and academic year. I truly appreciate the time and care he has dedicated to helping me succeed. I would also like to thank Chol Kaewwichit for his help in the lab.

The UROs scheme has been an enjoyable, formative experience that prepared me for future research.

Conclusion

A tooling factor of 66.7% was experimentally determined for one magnetron target, accounting for geometric asymmetry in the Nano-PVD system. This calibration enables improved process control and repeatability in thin film fabrication.

The attempted synthesis of CuAlFeS_2 via co-sputtering revealed key challenges. While EDS confirmed partial incorporation of Cu, Al, and S, Fe was not detected, likely due to its low sputtering yield and stronger binding within the ceramic target. S incorporation was also limited, consistent with its volatility and the absence of a reactive gas environment. These results indicate that alternative deposition strategies, such as chemical spray pyrolysis or reactive sputtering, may be required to achieve stoichiometric CuAlFeS_2 films. Future work will focus on determining the tooling factor for the other magnetron guns and validating the optoelectronic properties of the resulting materials for photovoltaic applications.

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