Advanced Calibration and Application of Quartz Crystal Microbalance in Atomic Layer Deposition

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Atomic Layer Deposition (ALD) is an appealing thin-film deposition method for synthesising high-quality surface and contact passivating stacks for photovoltaic devices. ALD allows for atomic scale tailoring of the deposited material towards desired properties such as work function and conductivity. Unfortunately, not all characterisation techniques which are used for other thin film deposition techniques can straightforwardly be used in ALD. For example, the Quartz Crystal Microbalance (QCM) technique has been designed for evaporation deposition (ED) in high vacuum environment, while ALD processes take place at significantly higher pressures in the range of 0.1 - 10 mbar. Assumptions which are valid in ED no longer hold in ALD systems, and thus resulting in inevitable measurement errors. Under high vacuum conditions, it can be assumed that the measured frequency change of QCM crystal resonator (ΔF) is only caused by the mass change of foreign layers deposited on the crystal surface (i.e. $\Delta F = \Delta F_m$). However, in a higher-pressure ALD chamber, the measured frequency change is attributed to: (1) the mass of foreign layers deposited on the crystal surface ΔF_m, (2) the chamber pressure ΔF_P, (3) the density and viscosity of the gas surrounding the crystal ΔF_η, and (4) the surface roughness of the crystal ΔF_r (i.e. $\Delta F = \Delta F_m + \Delta F_P + \Delta F_\eta + \Delta F_r$). In this work, we quantified all these individual contributions using a novel measurement procedure. This new calibration method is subsequently applied on the thermal ALD Al_2O_3 process using the non-pyrophoric precursor dimethylaluminum isopropoxide (DMAI) as the Al-precursor and H_2O as the oxidant. This novel measurement procedure allows us to fully utilise the advantage of high precision QCM data to monitor and analyse the atomic scale deposition processes and the physical properties of the functional thin film.

Figure 1 shows the ALD recipes for the QCM calibration, which includes a normal thermal ALD process for the raw QCM measurement and two non-deposition processes for the error determination. A 0.5 µg/cm² Al_2O_3 thin film was deposited on SiO_2 QCM crystal at 200 °C in 20 ALD cycles, and the other two ALD processes were set at the non-alternant pulses to determine the independent effects of DMAI and H_2O pulses on QCM. Ar gas was pumped into the ALD chamber for 5000 s to stabilise the QCM crystal resonator before the processes as shown in Figure 2 (left). The ALD pulse times were set to 0.2 s and 0.1 s for the precursor and the oxidant, respectively, and the ALD chamber was purged for 10 s after each pulse. During the whole processes, the QCM resonator frequency was monitored which can be converted into a relative mass using the Sauerbrey equation. *In-situ* Spectroscopic Ellipsometry (SE) was also used to extract the thickness, surface roughness, and optical constants of the synthesised thin film. Figure 2 (right) also shows the comparison of the raw QCM measurement and the corrected QCM measurement. The corrected QCM measurement was calculated by extracting the non-deposition QCM measurement from the QCM measurement taken when an ALD deposition takes.

As shown in Figure 2 (right), the raw QCM measurement was significantly biased during very short ALD pulses. Indeed, the corrected QCM measurement does show two sharp mass changes after the pulses indicating the actual instantaneous surface reactions. Even though the raw QCM measurement is able to determine growth-per-cycle (GPC, 1% difference compared to *in-situ* SE), eliminating these systematic errors allows us to fully utilise the advantages of the high precision (0.001 µg/cm²) of QCM for more advanced surface chemistry analysis.

The corrected high-precision QCM measurement was applied to investigate the growth characteristics and the properties of the deposited thin film. Firstly, the corrected QCM measurement provided precise information in mass gain and loss, which can help to analyse reaction probabilities during the deposition process. The results are found to be consistent with literature values as shown in Table I. Secondly, with *in-situ* SE measurements and corrected QCM measurements, we developed a model to accurately predict the true density of the film as shown in Figure 3. We validated this density model with literature reported data.
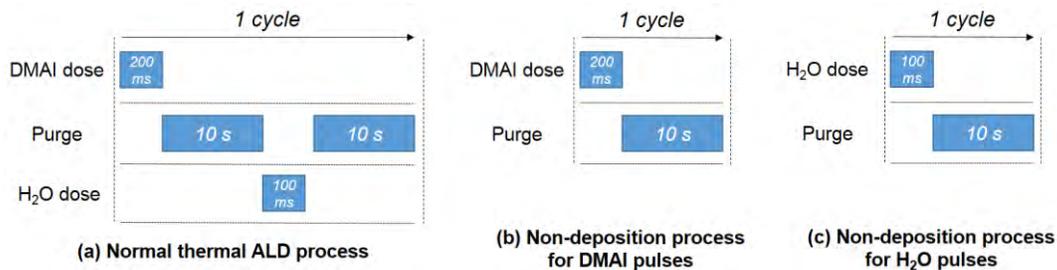

Figure 1. The recipes of the ALD thin-film-deposited process and the non-deposition process for QCM calibration.
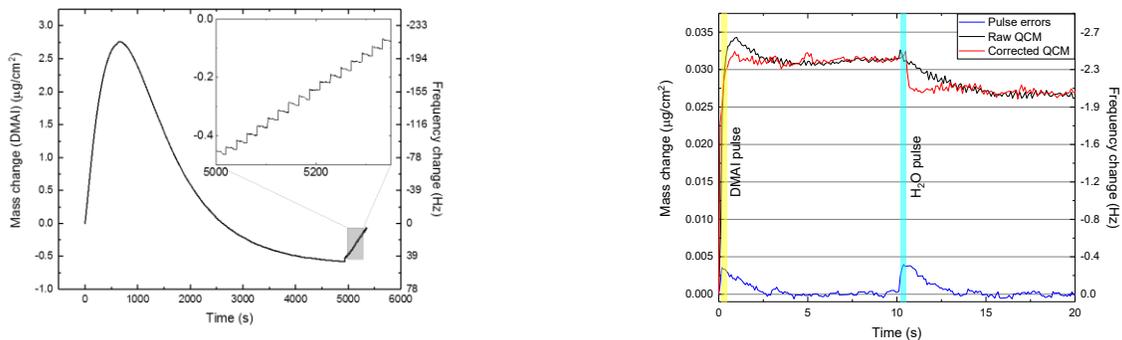

Figure 2. The raw QCM measurement of the complete normal ALD process including QCM stabilisation time (left), and the single-cycle comparison of the pulse errors, the raw QCM measurement and the corrected QCM measurement (right).

Table I. The reaction probability calculated from the known reaction energy barrier and deduced from the QCM measurements.

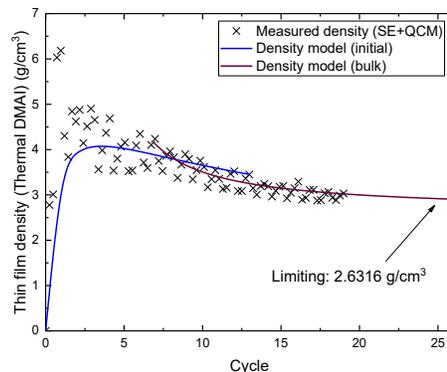| Bond breaking	Reaction formula	Reaction energy barrier [eV]	Reaction possibility by energy barrier	Reaction possibility by QCM
Al–C	$-OH + Al(CH_3)_2(O^iPr) \rightarrow -OAl(CH_3)(O^iPr) + CH_4$	~0.28	53%	58%
Al–O	$-OH + Al(CH_3)_2(O^iPr) \rightarrow -OAl(CH_3)_2 + HO^iPr$	~0.31	47%	42%

Figure 3. The *in-situ* density of thermal DMAI and the proposed density models.