Dissipative QCM

DETERMINING LAYER MASS DURING REPEATED LB-FILM DEPOSITION BY EX SITU MEASUREMENT OF RESONANCE FREQUENCY IN AIR

Introduction

Anything that has a mass can generate a response from a QCM sensor, which explains its wide range of applications. For example, the use of the QCM technique for monitoring thickness in metal evaporation and sputtering is widely known. In the same way the Dissipative QCM (KSV QCM-Z500) can be used to monitor the deposition of precisely defined thin (rigid) layers such as Langmuir-Blodgett films.

Figure 1 shows the basic principle of LB film deposition from a floating monolayer at an air-water interface. Using a hydrophilic substrate (like clean gold) a one molecule thick monolayer can be deposited in the first stroke followed by successive depositions of 2 monolayers per deposition stroke to form a uniform, thin (in most cases rigid) layer, the thickness of which increases for each deposition cycle.

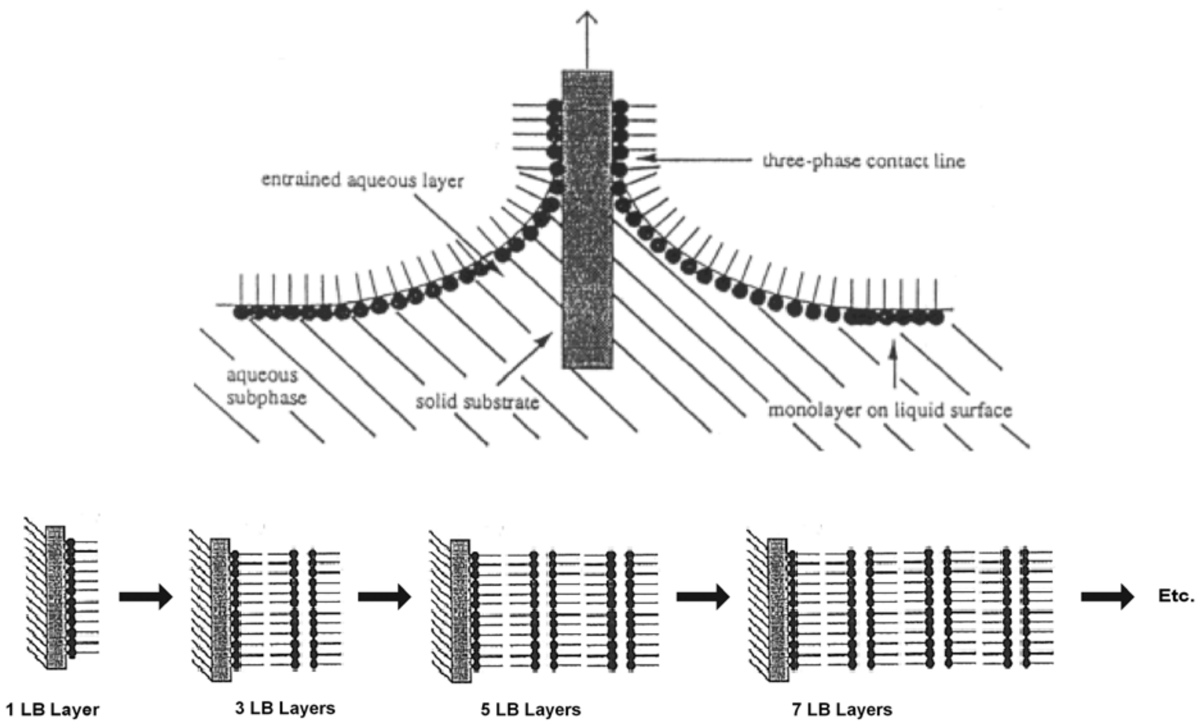

Figure 1 (Adapted from Adv. Coll. Interf. Sci. vol. 34 (1991) p. 343)

Experimental

The technique discussed above was used in the current example to build a multilayer structure on a gold-coated quartz crystal by successively depositing monolayers of Stearic Acid (SA, $C_{17}H_{35}COOH$). The frequency change induced after each deposition cycle of the floating monolayer was measured with Dissipative QCM. First, the resonance frequency of the clean gold-coated quartz crystal was measured in air in the standard QCM-Z500 measuring chamber. Thereafter, the crystal was removed from the measuring chamber, and one monolayer of SA was deposited, the frequency then determined in air as previously. The change in resonance frequency due deposition could then be determined. Subsequently, a bilayer of the SA monlayer was deposited on the crystal and the total decrease of frequency of the 3 deposited layers extracted. The same procedure was repeated until 45 layers of the SA acid were deposited on the quartz crystal.

The SA monolayers were deposited on the gold coated quartz crystal with a KSV Minitrough 2 film balance from a 10^{-4} M $MnCl_2$ subphase with pH ~ 6 at a constant surface pressure of 30 mN/m.

Results

Figure 2 below shows the *ex situ* frequency change for the measured overtones in air determined with the Dissipative QCM (KSV QCM-Z500) after deposition of SA monolayers on both sides of a 5 MHz quartz crystal. All overtones show a linear frequency change due to the increased number of deposited SA monolayers.

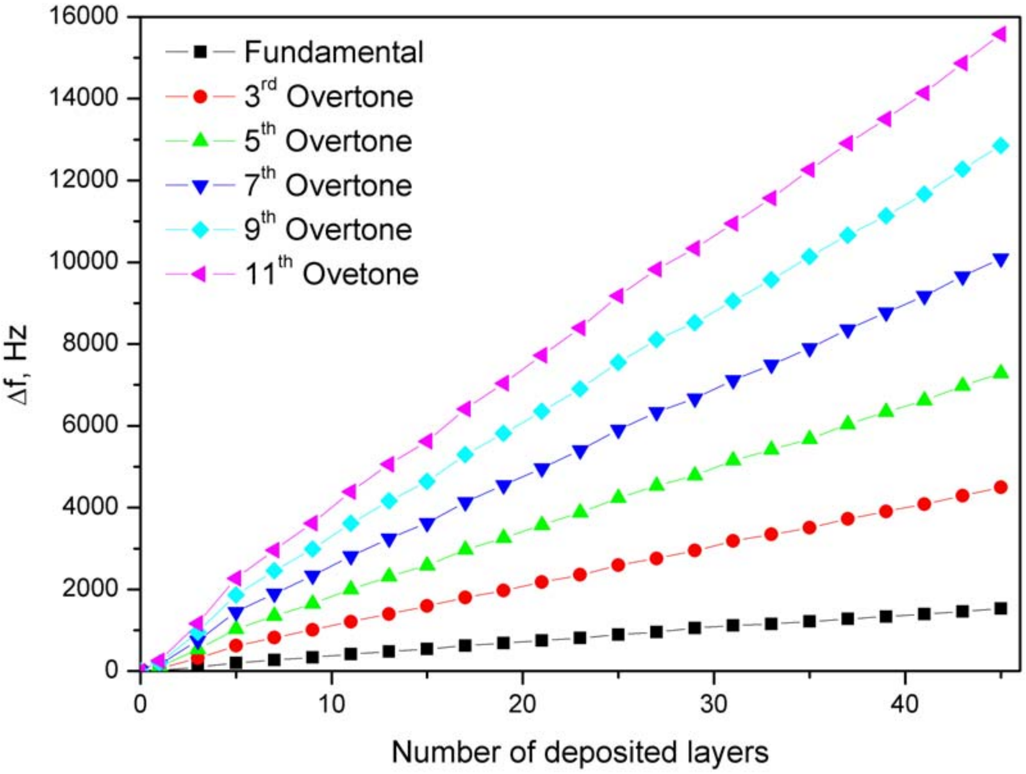

Figure 2

By using the data from Figure 2, and the area per SA molecule measured from the Langmuir compression isotherm i.e. 20 $Å^2$/molecule (Langmuir, vol. 10 (1994) p. 1592), the active electrode area on the quartz crystal 19.63 mm^2, and an average molecular weight of 343.5 g/mol of the Stearic acid – Manganese complex when 50 % of the SA monolayer is undissociated as in the conditions for the deposition in this case (Langmuir, vol. 10 (1994) p. 1592), the Sauerbrey equation predicts that 1 SA monolayer deposited on both sides of the quartz crystal should induce a 32.2 Hz (16.1 Hz for a monolayer on each side of the quartz crystal) change in frequency. This frequency change corresponds to a mass increase of ~ 285 ng/cm^2 for one monolayer on one side of the quartz crystal.

Figure 3 shows the excellent correlation between measured and predicted frequency change. The measured frequency change, averaged over all normalized overtones is plotted as the blue dotted line, and the predicted frequency change as open squares.

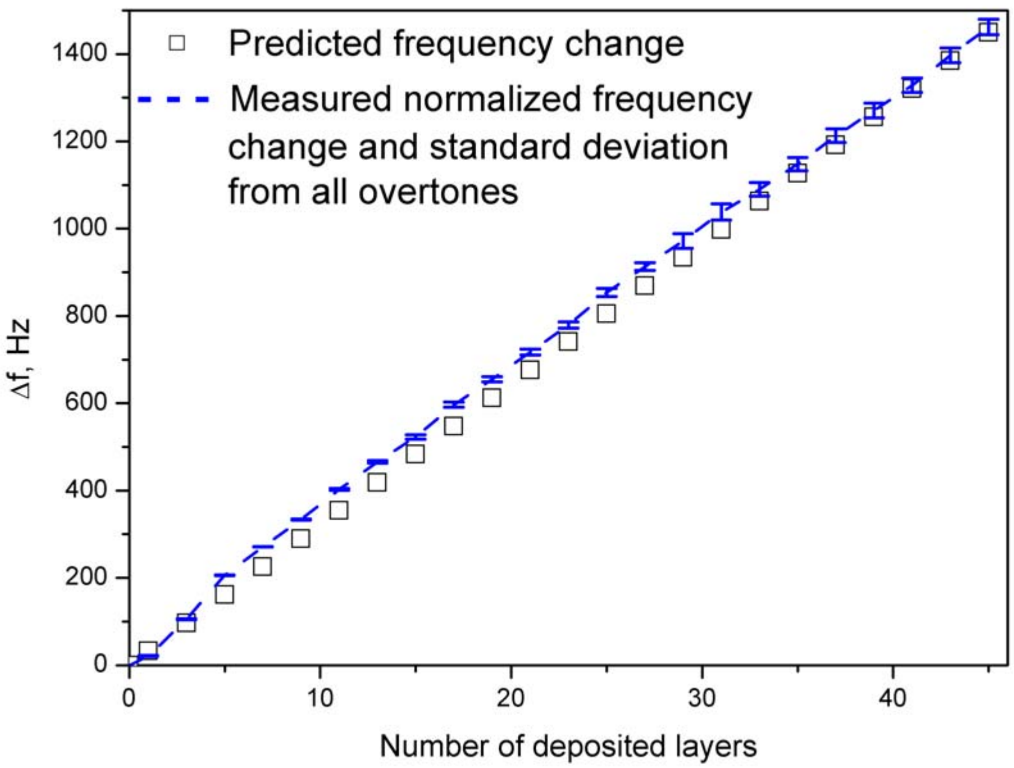

Figure 3

Conclusion

Dissipative QCM is an excellent tool for confirming the quality of LB deposited films, in terms of adsorbed mass. The measurement of both frequency and dissipation change at several overtones allows fitting to theoretical models, which can provide other important layer parameters such as thickness, viscosity and density.