Development of a quartz crystal resonator with a resonance frequency of 4 MHz

Atsushi ITO[*1]

[*1] Components Divison, ULVAC, Inc., 2500 Hagisono, Chigasaki, Kanagawa, 253-8543, Japan

A quartz crystal microbalance (QCM) is typically used to monitor the vapor deposition of organic materials, and QCM sensors feature a quartz crystal resonator with a resonance frequency of 5 or 6 MHz. When a metal or oxide film forms on a sensor, the rate at which the material adheres varies little. When an organic film forms on a sensor, however, the rate at which the material adheres varies considerably. This causes a problem since it greatly reduces the life of the quartz crystal resonator. The current work used several quartz crystal resonators with different fundamental frequencies to measure electrical and temperature characteristics during formation of an organic film. Results indicated that a quartz crystal resonator with a resonance frequency of 4 MHz or lower was better suited to sensing vapor deposition of an organic material than a resonator with a resonance frequency of 5 or 6 MHz.

1. Introduction

The Quartz Crystal Microbalance (QCM) method is capable of relatively easily detecting very small changes in mass. It allows for measurements not only in the gas phase but also in the liquid phase, so it is widely used for various kinds of sensors, such as gas sensors, film thickness sensors[1)], viscosity sensors[2–4)], chemical sensors, and biosensors[5, 6)] used to measure the interactions of DNA, protein and other biological materials.

In the past, 5 MHz or 6 MHz quartz crystal resonators were commonly used for QCM-based vapor deposition monitors. In organic EL manufacturing processes, QCM-based vapor deposition monitors are used to monitor the deposition rates of organic materials. However, when measuring the deposition rate of an organic material, it is necessary to frequently replace the quartz crystal resonator that is the detecting part of the sensor. This is because the measured deposition rate of an organic material greatly varies when even a thin film forms on the quartz crystal resonator, though this phenomenon is not seen with a metallic or oxidic materials.

To investigate the cause of the phenomenon, a study was conducted as reported herein by depositing organic material films and measuring the equivalent series resistance of the resonance frequency, R1, and the increase in half width at half maximum, ΔFw (Figure 1), which are the electric characteristics, and the thermal characteristics and changes in frequency due to thermal shock were measured by using sensors made of quartz crystal resonators with different fundamental frequencies.

2. Measurement Conditions

A typical material used to deposit organic films, Alq3, was used and ULVAC's Organic EL Manufacturing System, SATELLA, was used as the deposition system.

The 4 MHz and 5 MHz resonators used were ULVAC's AT-cut quartz crystal resonators with an outer dimension of ϕ12.4, while the 6 MHz resonators were ULVAC's AT-cut quartz crystal resonators with an outer dimension of ϕ14.

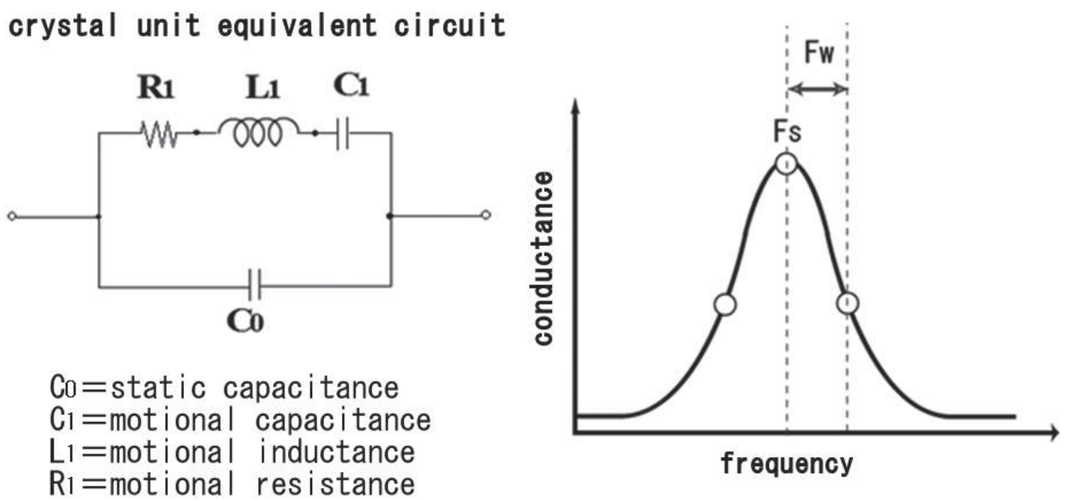

Figure 1 Crystal unit equivalent circuit and half width at half maximum ΔFw.

ULVAC's Quartz Crystal Deposition Controller, CRTM-9200, was used as the film thickness monitor.

A 30-W halogen lamp was used for the thermal shock measurements, and a Peltier thermostat was used for the temperature characteristics measurements.

ADVANTEST's Network Analyzer, R3754A, was used for electric characteristics measurements.

3. Results

Figures 2 and 3 respectively show the results of measuring R1 and ΔFw, by using the Network Analyzer, at the resonance frequency when a 60 μm organic film was formed on each of the quartz crystal resonators with fundamental wave frequencies of 4 MHz, 5 MHz and 6 MHz.

When a film is formed on a quartz crystal resonator, a smaller R1 and ΔFw leads to more stable deposition rate measurement. The figures indicate that the quartz crystal resonator with a fundamental frequency of 4 MHz or less

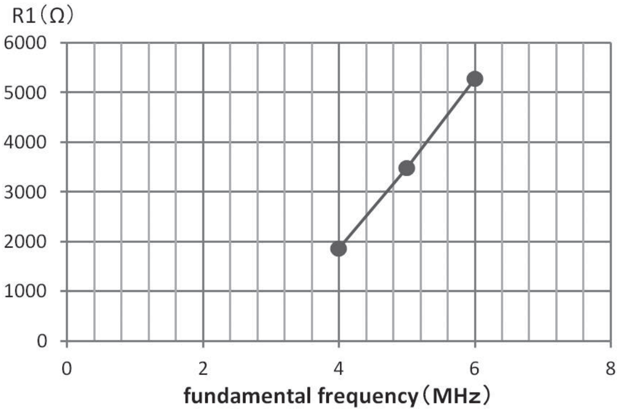

Figure 2 Relationship between the fundamental frequency and motional resistance R1 when an organic film of about 60 μm is formed on a quartz crystal resonator.

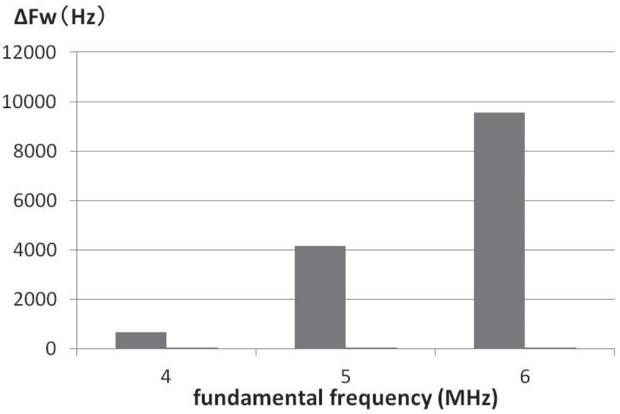

Figure 3 Relationship between the fundamental frequency and ΔFw when an organic film of about 60 μm is formed on a quartz crystal resonator.

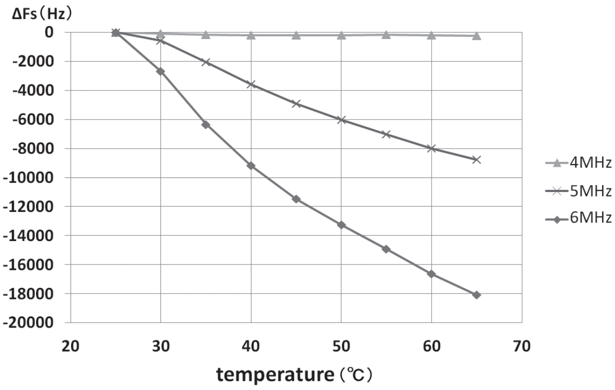

Figure 4 Temperature characteristics when an organic film of about 60 μm is formed.

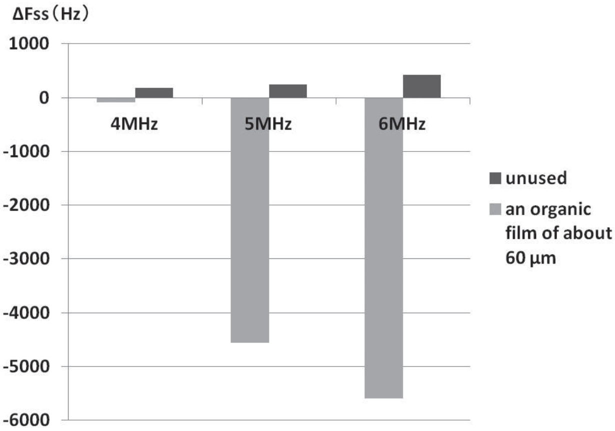

Figure 5 Change in frequency due to thermal shock when an organic film of about 60 μm is form.

is better for monitoring organic films than those with a fundamental frequency of 6 MHz or 5 MHz.

Figures 4 and 5 respectively show temperature characteristics, ΔFs, and changes in frequency due to thermal shock, ΔFss, at each fundamental frequency when a 60 μm organic film was formed on each quartz crystal resonator. The quartz crystal resonator with a fundamental frequency of 4 MHz exhibited smaller changes in frequency due to temperature change and due to thermal shock than the quartz crystal resonator with a fundamental frequency of 6 MHz or 5 MHz, and was found to have characteristics that vary little depending on temperature changes.

5 MHz and 6 MHz quartz crystal resonators have been widely used for QCM thickness meters for many years. However, it has become clear that 4 MHz quartz crystal resonators are more advantageous for organic film measurements in terms of stability of rate, service life and temperature characteristics.

Quartz crystal resonators with a fundamental frequency of 4 MHz are available from ULVAC as product UCR-4MAG-01[7] and can be used with the Quartz Crystal Depo-

Table 1　UCR Series Specification.

Model	UCR-4MAG-01	UCR-5MAU-01	UCR-5MAG-01
Recommended process	Organic film（OLED）	Metal and Optical film	
Frequency	4 MHz	5 MHz	
Diameter	ϕ12.4		
Electrode	Ag	Au	Ag
Controller	CRTM-9200	CRTM-6000G CRTM-9200	
Sensor	Single sensor （CRTS-4, 6, 0） Multi sensor （CRTS-12NS）	Single sensor （CRTS-4, 6, 0, 84, 86, 80, 4U, 6U, 84U, 86U） Multi sensor （CRTS-12NS, M6）	
Surface finish	Mirror finish	Standard Type	
Case	Carousel type case（10pcs）		
outline view			

sition Controller, CRTM-9200.

In conjunction with the launch of quartz crystal resonators with a fundamental frequency of 4 MHz, quartz crystal resonators with a fundamental frequency of 5 MHz with improved temperature characteristics were developed. These quartz crystal resonators are now available as part of the UCR Series. Table 1 shows their specifications.

References

1) C. Lu and O. J. Lewis 1972 Investigation film-thickness detaermination by oscillating quartz resonators with large mass load 1972 Appl. Phys. 43, 4385-4390
2) S. J. Martin, K. O. Wessendorf, C. T. Gebert, and G. C. Frye 1993 Measuring liquid properties with smooth- and textured-surfaceresonators Proc. IEEE Int. Freq. Control Symp. 47, 603-608
3) D. C. Ash, M. J. Joyce, C. Barnes, C. J. Booth, and A. C. Jefferies 2003 Viscosity measurement of industrial oils using the droplet quartz crystal microbalance Meas. Sci. Technol. 14, 1955-1962
4) A. Itoh and M. Ichihasi 2011 Separate measurement of the density and viscosity of a liquid using a quartz crystal microbalance based an admittance analysis (QCM-A) Meas. Sci. Tecnol. 015402 (6pp)
5) Y. Ebara and Y. Okahata 1994 A Kinetic-Study of Concanavalin-A Binding to Glycolipid Monolayers by Using a Quartz-Crystal Microbalance J. Am. Chem. Soc. 116 25 11209-11212
6) A. Itoh and M. Ichihashi 2008 A frequency of the Quartz Cystal Microbalance (QCM) that is not affected by th viscosity of a liquid *Meas. Sci. Tecnol.* 19, 075205 (9p
7) Ito, Fukao, Kobayashi: Japan Patent JP6078694

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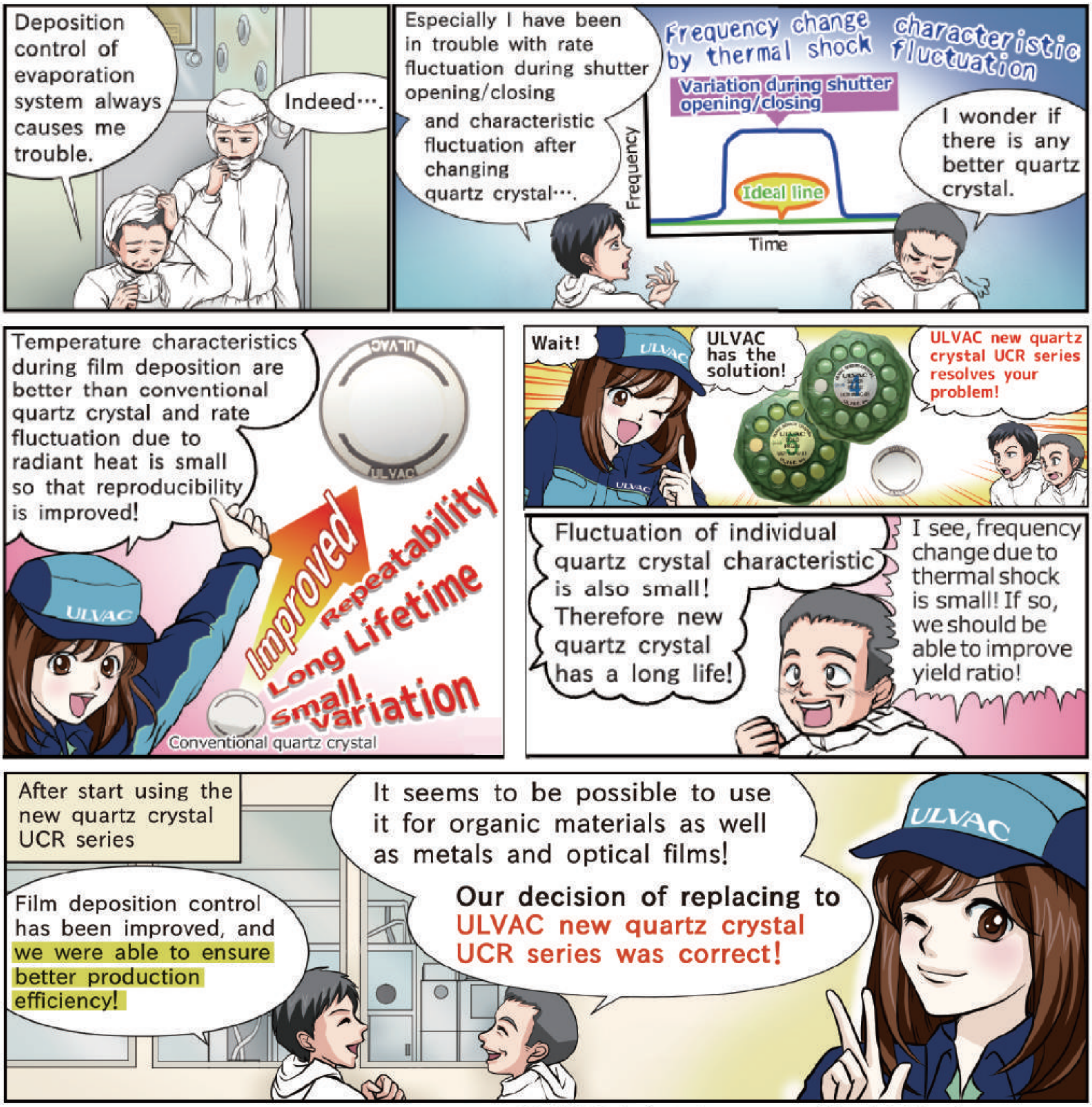

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www.ulvac.co.jp/en

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·USA : ULVAC Technologies, Inc. TEL +1-978-686-7550
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·SINGAPORE : ULVAC SINGAPORE PTE LTD. TEL +65-6542-2700
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