COMPUTER CONTROLLED QUARTZ MICROBALANCE SYSTEM FOR THIN FILM VACUUM DEPOSITION

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Two-channel quartz microbalance monitor for in situ thickness measurement based on PC computer was constructed and tested. The thickness monitor is galvanically insulated from the vacuum device up to voltages of 2.5 kV. The computer software implements frequency-to-thickness conversion and data smoothing by numerical integration and digital band-pass filtering. The frequency instability of the base oscillator is less than ±0.5 Hz (±0.12 ppm). The device was tested by simultaneous vacuum evaporation of the polyimide precursors – piromellitic dianhydride and oxydianiline. Deposition rate with instability less than ±5% was achieved.

Keywords: quartz microbalance monitor, thin film thickness measurement, computer data acquisition

1. INTRODUCTION

The *in situ* thickness measurement is of the main importance during the vacuum deposition of organic thin films. Two basic methods are often used for an *in situ* thickness monitoring. The first one is based on the measurement of the optical transmission of the deposited film. This method could not be always used, e.g. in case of nontransparent of fully transparent films. More simple method is based on the property that the resonance frequency of AT-cut quartz crystal is very sensitive to addition of mass on its surface. First quantitative estimation of this effect was done by Sauerbrey in 1959 [1]. Later quartz-crystal microbalnce (QCM) devices were developed and extensively used for measurement of small mass changes in thin-film science and technology [2].

The deposition of the organic materials exhibits some specific features, which sometime needs flexible data processing. For the majority of organic substances a sublimation process takes place. This leads to a fluctuation in the deposition rate of almost random character. This effect could be successfully suppressed by integration or using of different filters. All these corrections could be easily done by flexible software based on PC computer.

The application of QCMs has not been restricted to thin film thickness measurements in vacuum. It was verified experimentally [3] that quartz resonators

could also respond to properties of a contacting liquid. These observations opened the way for investigation of properties of liquids [4, 5] or films immersed in liquids. Interfacial slip [6], lossy adsorbates [7], film rheology [8, 9], dispersion in colloidal films [10], conductive fluid [11], conducting polymer films [12], protein multilayers [13] and phase transitions in liquid crystals and lipid multibilayers [14]. On the base of this information sophisticated sensors, e.g. electronic noses [15, 16] can be developed. These different tasks based on the same principle only required different construction of the crystal measuring heads and different data processing. The last one could be easily achieved by computer.

This work presents construction and testing of quartz microbalance device for *in situ* thickness measurement, based on PC computer.

2. Outline of the Theory

The quartz microbalance thin film monitor is based on the property of an oscillating quartz crystal to decrease its resonant frequency upon an influence of added mass. This effect is used to monitor the deposition rate and film thickness during vacuum coating.

In 1959 Sauerbrey [1] gives first quantitative estimation on the dependence between the frequency shift and the change in the mass due to the coating material:

$$\frac{M_f}{M_q} = \frac{\Delta F}{F_q} \quad \text{or} \quad M_f = M_q \frac{\Delta F}{F_q}, \qquad (1)$$

where M_f is the mass of the coating, M_q - mass of the quartz prior to coating, F_q - frequency prior to coating, F_c - frequency after coating and $\Delta F = F_f - F_c$ is the frequency shift due to coating. If the following are now applied:

$$M_f = (M_c - M_q) = D_f \rho_f A \quad \text{and} \quad M_q = D_q \rho_q A, \qquad (2)$$

where D is the coating thickness, ρ - density and A stands for the coated area, then:

$$D_f = \frac{F_q}{F_q} D_q \rho_q \frac{\Delta F}{F_q \cdot \rho_f} = K \frac{\Delta F}{\rho_f} \qquad (3)$$

with

$$K = \frac{D_q F_q \rho_q}{F_q^2} = \frac{N_{AT} \rho_q}{F_q^2}, \qquad (4)$$

where $N = F_q D_q$ is the frequency constant (for the AT cut quartz N_{AT} = 166100 Hz cm) and $\rho_q = 2.649\ g/cm^3$ is the density of the quartz. Here index q stands for the state of the "uncoated quartz" and c for the state after "frequency shift due to coating". Finally once can get:

$$D_f = K \frac{\Delta F}{\rho_f}. \qquad (5)$$

According to this equation, a crystal with a starting frequency of 6.0 MHz decrease its frequency with 2.27 Hz after coating with 1Å of aluminum (ρ_f = 2.77 g/cm^3). This example shows the high sensitivity of the method.

3. Block Diagram and Device Description

3.1. Hardware

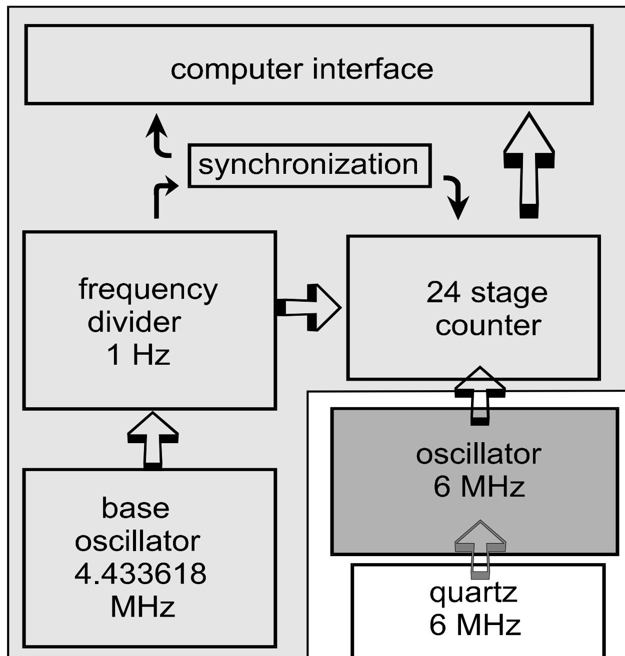

Fig. 1. Block diagram of the quartz microbalance thin film thickness monitor

The block diagram of the device is presented in Fig. 1. It contains of base oscillator, frequency divider, counter, synchronization circuit, measuring oscillator, measuring quartz and computer interface circuit. All blocks, except the measuring oscillator and quartz are built on a board inside the computer and connected with the motherboard via ISA bus. All blocks of the system inside the computer are powered from the computer power supply (+5V). The power consumption of the board is less than 2.5 VA.

The base oscillator is realized with P 8284A clock generator and 4.433618 MHz quartz crystal.

The sampling rate is obtained dividing the frequency of the base generator with a cascade of decade counters. The waveform of the sampling rate of 1.36 s is presented in Fig. 2. The counting of the frequency, which is related to the film thickness measured, is allowed during the period of 1.08 s. In this way a resolution better than 1 Hz is provided. The rest of the time of 0.28 s is used for synchronization. The synchronization unit implements the following tasks:

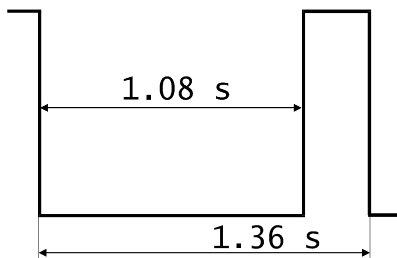

Fig. 2. The waveform of the sampling rate

i) Stops the pulse counting when the period of 1.08 s expires.
ii) Reports that the data are ready on the bus to cause the data acquisition by the computer.
iii) Clear the counters after the data acquisition occurs in a way to prepare the next measurement.

Commercially fabricated gold-coated 6 MHz INFICON quartz crystal placed inside the vacuum system is used as measuring head. It should be connected to the oscillator with a coaxial cable of less than 1 m length to provide stable oscillations and decrease of the noise. The output signal of the oscillator is transferred to the computer via high-speed response photocoupler, which provides insulation voltage between the vacuum device and the computer of 2.5 kV. The pulse formation before the counting was done by passing the signal trough a Schmitt trigger. The frequency

counting was implemented cascading two 12 stage binary counters. Finally the counted numbers are transferred to the PC via edged-triggered D-type flip-flops.

3.2. Software

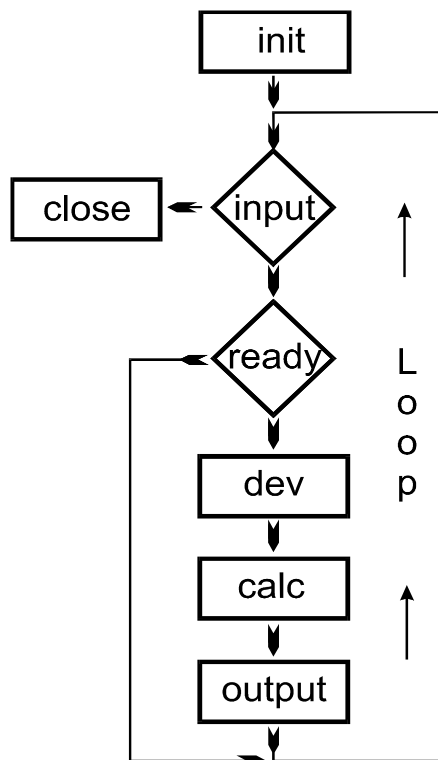

Fig. 3. Block-diagram of the software

The program for the data acquisition is written in object oriented Pascal. After the program starts an initialization of the measurement is implemented, e. g. reading the configuration file, initialization of the board, calculation unit and the output. After that the measuring loop is activated. The first step of the measurement is checking for an operator's command from the keyboard or mouse. If there is no request for exit the program checks the "data ready" flag. If the data are ready on the bus the program reads the data from the board then reads the system clock to get the time of the data reading. The calculation unit makes first the frequency-to-thickness conversion according to Equations 4 and 5. Then an integration of 5, 10 or 15 measured points is done to decrease the noise. To reject the uncorrelated noise during the integration a digital band-pass filter can be activated. The width of the band-pass filter can be softwarely adjusted. Finally the output unit saves the measured data in a file and plots a graph. In this way the measured and integrated deposition rate (in angstroms per second), the film thickness (in kiloansgstroms) and the XTAL parameters (in percents) are displayed and saved.

3. Testing and Application

In Fig. 3 the stability of the frequency of the base oscillator is presented. The measured frequency of the oscillator differs with 0.04 % from the frequency of the quartz used (4433618 Hz). This constant error could be connected with the internal capacitance of the P 828 chip. As the film thickness is calculated from the difference between two adjacent frequency readings this error is not of major importance. The measured data are plotted with squares. It could be seen that the maximum error of measurement is less than ±1 Hz (±0.23 ppm). The continuos (the spline interpolation of the data) presents the long-time stability of the device, which is less than ±0.35 Hz (±0.08 ppm). This error could be related to the temperature drift of the oscillator frequency. The main important parameter, which is related to the measurement, is the maximum error between two adjacent frequency readings. It is less than ±0.5 Hz

(±0.12 ppm). This error is less than the error of the measuring INFICON quartz crystal (±0.18 ppm), therefore the base oscillator fulfilled the requirements of the accuracy of the measurement.

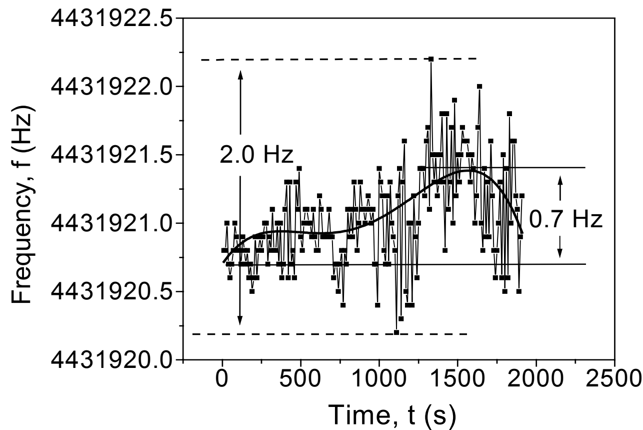

Fig. 4. Frequency stability of the base oscillator: squares – the measured data; continuos line – spline interpolation of the data

The device was implemented in two-channel modification and tested by co-evaporation of the polyimide (PI) precursors – piromellitic dianhydride (PMDA) and oxydianiline (ODA). The PMDA and ODA precursors are deposited by sublimation in vacuum at low temperatures (about 120°C). The sublimation process leads to an instability of the evaporation rate thus makes the control of the stoichiometry rather difficult [17].

From one side high stability of the evaporated flow could be achieved by usage of effusion (Knudsen) evaporation sources [18], where the volume of the vessel is large compared to the size of the evaporation hole. From the other side this is the accurate rate control, which could be achieved by the computer controlled rate measurement including integration and using of different filters.

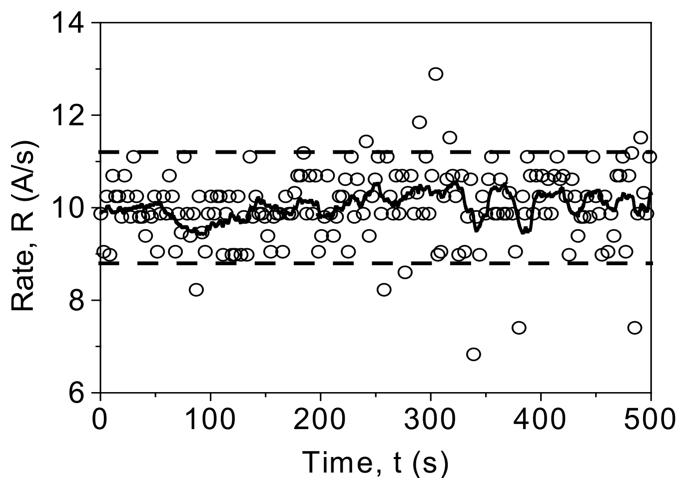

Fig. 5. Stability of the sublimation rate of PMDA precursor: circles – the measured data, continuous line – the curve after integration of 10 points, dash lines present the digital band filter applied

In Fig. 5 the sublimation rate of PMDA monomer as a function of the time is presented. The measured points are presented with circles. For a seek of clarification only half number of the measured points are plotted. It can be seen that the measured data are scattered mainly within a rate interval from 9 to 11 Å/s. This scattering could be related to the fluctuation of the evaporated flow. As these data have clear physical meaning they can be smoothed by integration. The integration is applied in the band between the dashed lines. The sublimation rate after integration of 10 measured points is plotted with continuous line. After the

integration the instability of the evaporation rate is less than ±0.5 Å/s. There are several points outside of the band of integration which could be connected with accidental disturbances. This noise very probably cannot be correlated with the process of sublimation. The uncorrelated noise is canceled by the digital band-pass filter (the dashed lines), which is included in the measured software.

CONCLUSION

Two-channel quartz microbalance monitor for *in situ* thickness measurement based on PC computer was constructed and tested. The device provides insulation voltage between the vacuum setup and the computer of 2.5 kV. The instability of the base oscillator is less than ±0.55 Hz (±0.12 ppm). The software provides numerical integration and digital band-pass filtering. Deposition rate with an instability less than ±5% was achieved.

ACKNOWLEDGMENTS

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