

Real Time Detection of Chemical Contaminant from Equipments Using QCM (Quartz Crystal Microbalance) Monitoring Technique

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Abstract – Sequence dependent contaminant release from LSI fabrication equipments are detected by means of QCM (Quartz Crystal Microbalance) monitoring system. This system is small, easy to handle, high sensitivity, reasonable cost, and will lead a powerful way to detect the origin of airborne chemical contamination in the advanced device fabrication plant.

INTRODUCTION

In recent days, chemical contamination control in device fabrication process becomes more and more important according to the scale reduction of designing rules [1]. Airborne chemical contamination is one of the defect sources in the advanced device fabrication process. But because of low concentration of contaminants in clean room atmosphere, it has been quite difficult to specify the origin of chemical contamination. As for air sampling analysis, in order to condense the contaminants to detectable amount, long-time cumulative sampling has been needed [2]. Therefore, the obtained data have been in principle short of time-dependent information.

We have been extending the application of QCM (Quartz Crystal Microbalance) to the detection of chemical contaminant release from fabrication equipments. The advantage of using QCM is that it can provide real-time quantitative information with high sensitivity [3]. By comparing the QCM data with logged process sequence, we can specify the origin of chemical contamination. Since the sensor head of the QCM is small, it can also be set inside of the equipment. Furthermore, semi-qualitative analysis can also be made by changing the material of the QCM sensor surface. After use, the sensor surface is analyzed by XPS and Raman spectroscopy in order to specify the deposited compounds. These data also provide valuable information.

In this paper, we will demonstrate the usefulness of QCM in the area of airborne chemical contamination control in fabrication process.

EXPERIMENTAL

Basis of using QCM in the detection of airborne chemical contamination

In 1959, Sauerbrey developed a relationship between the mass of films deposited on quartz crystals and the change in resonance frequency [4,5]. According to the relationship,

the change in resonance frequency of the quartz crystal Δf can be expressed as:

$$\Delta f = -\frac{f^2 \Delta m}{N r A} \quad (1)$$

where, f = original resonance frequency of the quartz plate, Δm = mass of the deposited film, N = frequency constant (0.1679 MHz cm⁻¹ for AT-cut quartz crystal), r = density of the quartz plate, A = surface area of the quartz plate. Substituting values for the other constants, a final equation is obtained as:

$$\Delta f = -\frac{2.3 \times 10^6 f^2 \Delta m}{A} \quad (2)$$

where, Δf = change in resonance frequency due to the surface deposition (Hz), f = frequency of the quartz plate before deposition (MHz), Δm = mass of the deposited matter (g), A = area of the surface (cm²). Eq. (2) indicates that a 25 MHz crystal would have the mass sensitivity of *ca.* 1 ng cm⁻² Hz⁻¹, and that the crystal may be used as the microbalance to weight the mass of the deposited matter on the surface of the crystal. Since the mass of the deposited matter is in equilibrium between the surface and atmospheric concentration, the crystal can also be used as the sensor for monitoring the atmospheric gas concentration.

The QCM system

The QCM system used in this study consists of three parts; five sensor heads (containing quartz crystal oscillators), frequency counter unit, and data logger PC. The quartz crystal oscillators, which have the resonance frequency of 25 MHz (Halloran Electronics Inc., Hachioji, Japan) are used in bare form (not canned). Each oscillator is set in the cylindrical housing made of aluminum (30 mm in diameter, 45 mm in length), and connected to the frequency counter unit (home-made) with coaxial cable of 10 m long. The frequency data are transmitted to the mobile PC (Fujitsu) *via* RS-232C interface, and averaged and logged every three minutes. The footprint of this system is very small as *ca.* 15 × 20 cm, we can set it in the vicinity of the fabrication equipments easily.

We use two types of quartz crystals which have silver and gold surfaces. By changing the surface material, semi-qualitative information may be expected. The fundamentals of sticking behavior over these sensors will be published in a separate paper of this symposium by one of us.

Sensor Setting

We select two types of typical fabrication equipments; oxidation furnace, and photo resist coating/developing system. The former is known to be very sensitive to chemical contamination, and the latter uses many kind of chemicals. As for photo system, we focused on two systems which belong to different air supply system each other.

The sensor heads are set on the frame of the equipments with tin wire.

RESULTS AND DISCUSSION

Oxidation furnace

Fig.1 shows the changes in frequency of QCM set around the oxidation furnace. Material of the sensor surface is silver. As clearly seen, all traces consist of two components; constantly increasing component, and spike-like component. This means that surface deposition with constant deposition

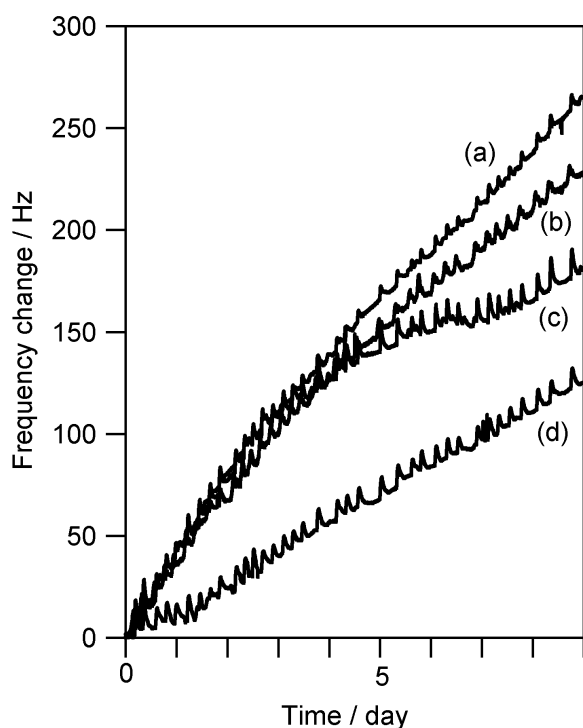


Figure 1. Frequency curves of QCM set around the oxidation furnaces plotted vs time. Traces (a)-(d) correspond to the sensors set at different positions of the equipment. Each curve consists of two types of components; spike-like, and constant increasing. Least square fittings of the curves (a)-(d) to linear line give the deposition rates of 14, 12, 9 and 7 $\text{ng cm}^{-2} \text{day}^{-1}$, respectively.

occurs simultaneously. Since it is well known that many kinds of hydrocarbons exist ubiquitously in atmosphere, the constant increasing component may be ascribable to this. But causing of absorption/desorption behavior remains unknown.

In Fig.2(b) and (c), closer view of the QCM curves appeared in Fig.1 are plotted. One can notice a timing delay of the peak between two traces. The sensors corresponding to (b) and (c) are set at different position of the equipment. The sensor (b) is set in the vicinity of the furnace, and is exposed to the exhaust air from the furnace directly. The sensor (c) is set at the foot of the equipment outside of the body.

In order to unveil the origin of absorption/desorption behavior, we analyzed the logged process sequence of the oxidation furnace. We focused on the temperature change of the furnace, and the timing of the loading-out of hot wafers. The results are depicted in Fig.2. Note two apparent coincidence. One is between the furnace temperature (trace a) and trace (b), and the other one is between trace (c) and the loading-out of hot wafers from furnace (vertical dotted lines). These observations suggest that thermal radiation from hot furnace and hot wafers causes gas releasing from this equipment, and the furnace and wafers heat up different area of the equipment each other.

The candidate for thermally desorped compounds are out-gas from painting material, sealing rubber, and airborne organic compounds accumulated on the surface of the equipment when the furnace is cold. But details are not clear at present stage, further analysis may be needed such as air sampling simultaneous to the temperature rising of the furnace.

Photo resist coater/developer system

On the other hand, monotonous increasing in frequency change is observed in photo resist coater/developer system as seen in Fig.3 (c) and (d). This means that constant and sequence-independent release of contaminants is occurred in this system. The deposition rates are found in the range of 3-32 $\text{ng cm}^{-2} \text{day}^{-1}$, these values are twice or thrice larger than that observed in the case of oxidation furnace mentioned in the previous section. These high deposition rates are thought to be attributable to the chemicals used in this system. We conducted the air sampling analysis using TENAX-TA/GC-MS system. As a result, we found Propylene Glycol Monomethyl Ether Acetate (PGMEA) used in this system as an organic solvent of photo resist and thinner. Since the PGMEA has moderate evaporation rate, vaporized PGMEA gas is thought to be released from the photo system.

The surface of the sensor head (silver) set around the photo resist coater/developer system is found to be tarnished. From the XPS and Raman spectroscopic analysis of the surface, some organic compound (including carboxylic acids) are found in addition to the corrosion products such as AgCl , Ag_2S and Ag_2O . These data imply that corrosion of silver surface is promoted under presence of hydrolysis product of PGMEA such as acetate CH_3COO^- .

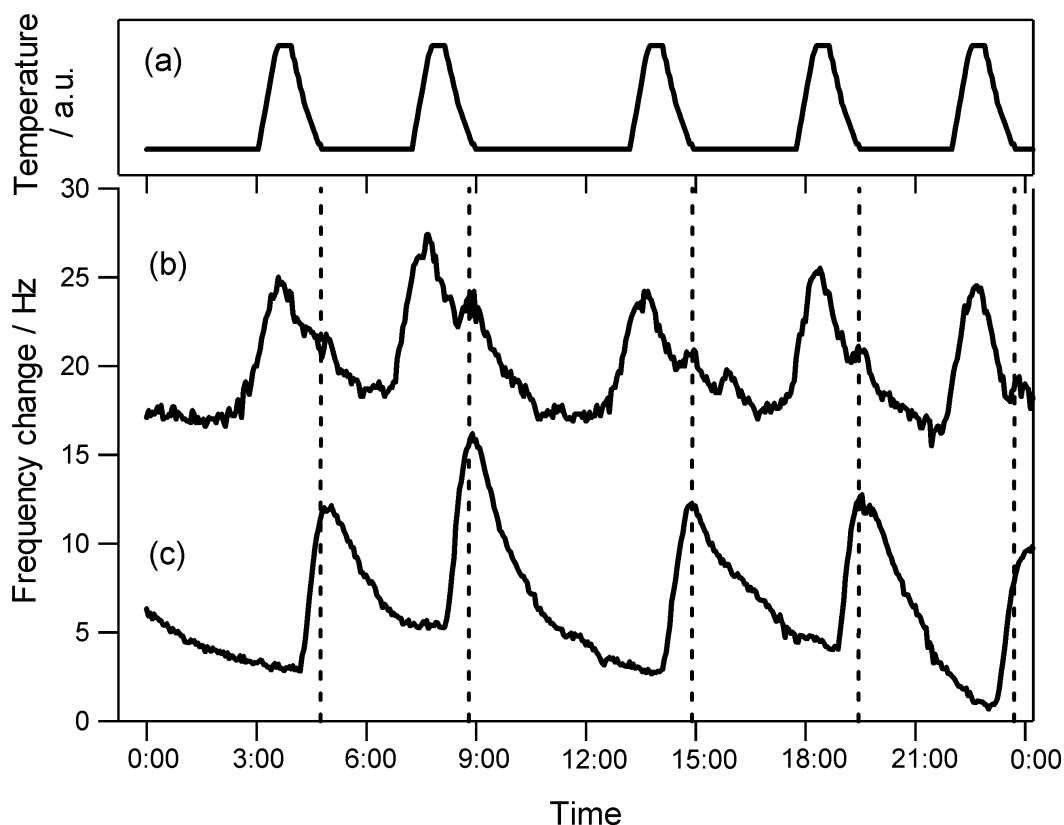


Figure 2. Closer view of the frequency curves appeared in Fig.1 [(b) and (c)]. In order to emphasize the short cycle pattern, the constant increasing component is subtracted arithmetically. The temperature of the oxidation furnace is also plotted schematically in trace (a). The dotted vertical lines indicate the timing of loading-out of hot wafers from oxidation furnace. Note the coincidence between the peak-top of trace (c) and the loading-out of hot wafers. Another coincidence between the temperature of the furnace and trace (b) is also seen.

Contaminant intake from OA

Fig. 3 shows the QCM data in long time period (*ca.* 50 days) obtained from two different photo system operated under discrete air supply system. Although the curves are nearly linear, but on closer inspection we find some humps occur simultaneously in both system. Because two air supply systems are discrete, the causing of humps may originate from out of plant.

For comparison, atmospheric concentration of NO_2 and NO in outer air are plotted in the same time axis in Fig. 3(a) and (b). (These values are measured by Saltzman method.) We can notice a coincidence between the humps in QCM curves and rising in NO_x concentrations. These observations imply that the QCM with silver surface have sensitivity to the nitrogen oxides. But since there are some similarity in the concentration curves of NO_2 and NO , we are not able to tell which one is the true causing of the humps at present stage.

Difference between silver and gold surfaces

In Fig.3(c), QCM data obtained by the crystals with gold surface are also plotted (the lowest trace). This curve has

some substantial differences from the curve taken by the crystals with silver surface. One thing is that the deposition rate (= slope) is very low as one thirds of the silver one. The other thing is that the gold one is nearly insensitive to the nitrogen oxides. These differences may be attributable to the chemical affinity (= binding energy) between the surface and sticking molecules, but the sticking mechanism is so complicated that we cannot explain these behaviors clearly at present stage.

In fact, semi-qualitative analysis will be possible by controlling the affinity between the surface and sticking molecules by changing the material of the surface. Since this application is not so practical now, more elaborate studies should be welcome.

SUMMARY

This study showed that the QCM was useful to specify the origin of chemical contamination. Time dependent information given by QCM monitoring and qualitative/quantitative information given by conventional analytical methods are complementary each other, and combining of both methods will lead a new way to specify the origin of airborne chemical contamination in fabrication

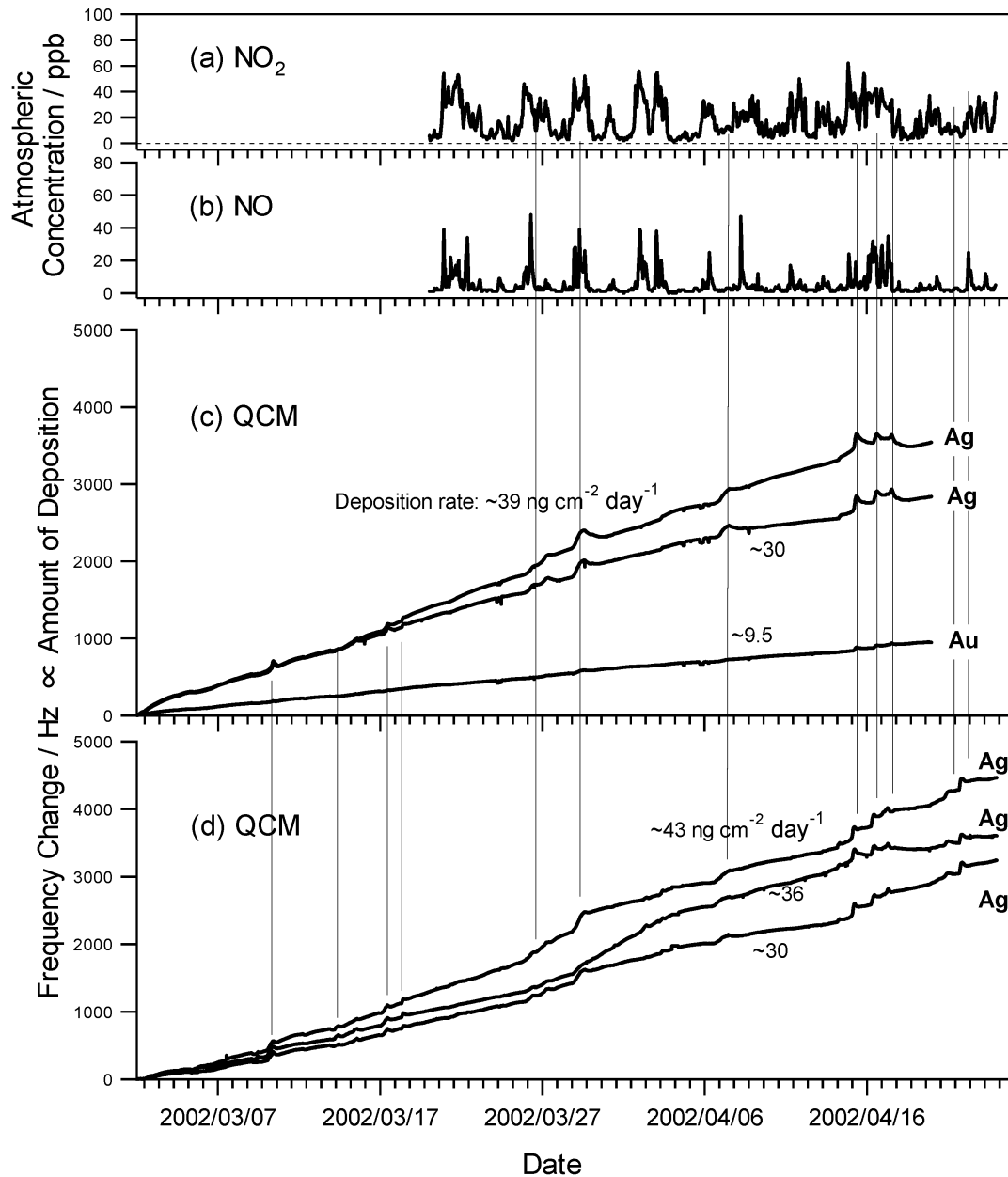


Figure 3. Frequency curves of the QCM set in the vicinity of two photo-systems operated under discrete air intake/conditioning system [(c) and (d)]. For comparison, atmospheric concentrations of NO₂ and NO (obtained from Mie prefectural air pollutant monitoring system located several kilometers from the plant) are also plotted [(a) and (b)]. Note the coincidence between the humps in frequency curves and rising in NO_x concentration curves.

process. Furthermore, since the QCM system is small, easy to handle, with reasonable cost, there may be many kind of applications.

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