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The Optical Behavior of Thickness-Shear-Mode Quartz Resonator

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1. Introduction

Recently, the analytical technology has been improved or newly developed as to the incremental requirement for electro-chemical phenomena at the interface. One of these research aspects, the quartz crystal microbalance(QCM) technology has been sophisticated one due to its high mass resolution. As it represents mass sensitivity of nano gram, the application area of QCM has been expanded as mass detector[1]. For past decades, many researchers have tried to expand the applicable area of QCM by studying its vibrational motion. Some results make it possible to operate in contact with liquid, enabling to enlarge the QCM application area [2]. One of main aspects in these studies is to be progressed on the basis of its electrical equivalent circuit[3-4]. Therefore, it is essential to understand the vibrational motion by its equivalent circuit, making it possible not only to find new analytical parameter, but also to obtain more precise information about the reaction at the interface or electrode surface.

In this paper, we will report the optical process of merocyanine dye LB films by UV spectroscopy, AFM, and quartz crystal resonators(QCR) method. The electrical behaviors of QCR deposited with dye LB film will be discussed as to the spectroscopic changes of dye LB film under UV irradiation to investigate possible application to optical analysis using QCR.

2. Experimentals

The amphiphilic merocyanine dyes were obtained from Hayashibara Biochemical Laboratories(Japan). When merocyanine dyes are deposited by LB method, fatty acid is mixed to improve their structural stability. Also, we could obtain a quantitative control of the spectroscopic characteristics of dye LB film by mixing fatty acid or changing the number of layer. The cadmium-containing buffer solution (0.4mmol/l) was used as subphase to form J-aggregate in air/water interface. For the LB film deposition, moving wall barrier type trough (NL-LB200 -MWC, Japan) was used. The 9MHz AT-cut quartz crystal was used to carry out QCR measurement. FIGURE 2 shows the experimental set-up for optical behavior of QCR with dye LB film. The optical characteristics of dye LB film were evaluated by UV spectroscopy (Fastevert S-2600, Japan). The morphological changes, which has been regarded as an important factor to affect the vibrational motion of QCR[7], was also observed and compared with the QCR data.

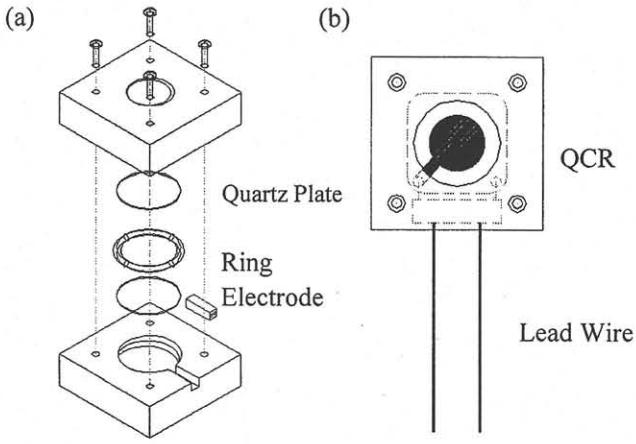

Fig. 1 The optical cell for QCM measurement ; (a) side view, (b) top view

3. Results and Discussion

Fig. 2(a) shows the frequency dependent conductance and susceptance plot before and after UV irradiation. The resonant frequency moved to low frequency range. Conventionally, it has been known that the decrease of resonant frequency was originated from the mass loading. Note that resonant frequency can be changed without considering mass loading process. The decrease of resonant frequency was proportional to the irradiation time and then saturated(See Fig. 2(b)). In Fig. 2(b), we should attend that the frequency shift was dependent on mixing ratio with fatty acid. We can control spectroscopic characteristics of dye LB film. The absorption peak at J-band was linearly decreased as to mixing the fatty acid. Thus the frequency shift of each sample can be represented by the mixing ratio with fatty acid, that is, absorption peak. The higher absorption peak of aggregated dye LB film can lead to the more frequency shift of QCR. They showed the quantitative relationship between frequency shift and absorption peak, which mean the application possibility of QCR to optical analysis.

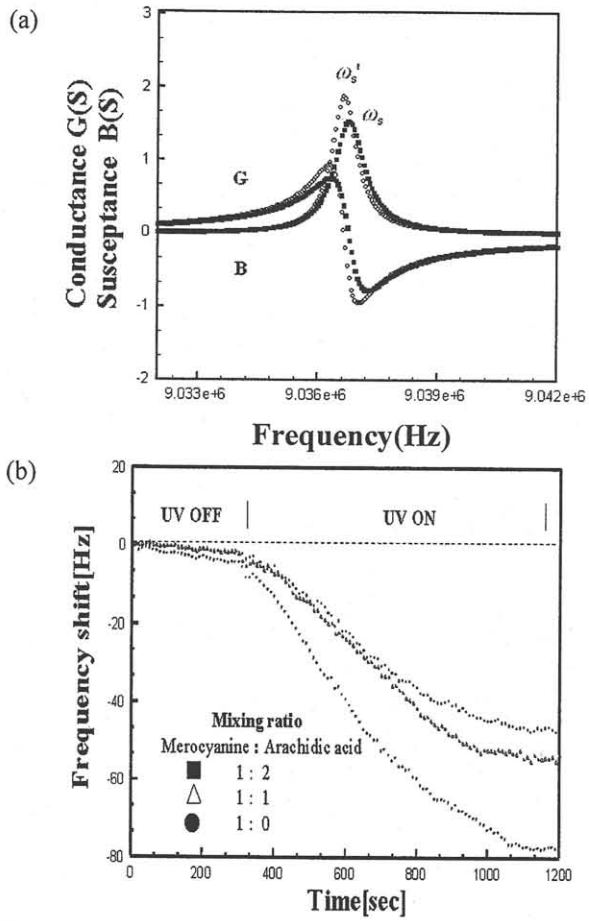

Fig. 2 The conductance and susceptance (a) and resonant frequency behavior(b) under UV irradiation.

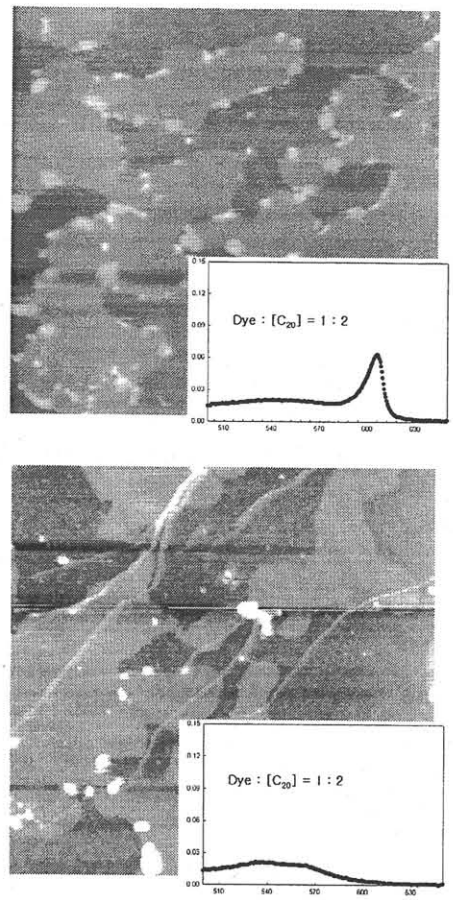

Fig. 3 The surface morphology change before(top) and after(bottom) UV irradiation.

To explain the frequency shift, we investigated the surface morphology changes. Fig. 3 shows the surface morphology changes before and after UV irradiation. There exist circular domain, which can be considered as aggregated dye structure, on the irregular background. The domains had different size as to the mixing ratio of arachidic acid and its high was about 40~50(Å) higher than that of monolayer. This 3-dimensional structure by the formation of the aggregate structure were reported by some researcher[5]. Their roughness on the top was 0.27[Å], which mean very homogenous structure. After UV irradiation, these domains were disappeared or their size was decreased. Thus we suggest that morphological changes by UV irradiation or the dissociation of J-aggregate can affect the vibration motion of quartz crystal[6] and originate changes in resonant frequency.

4. Conclusions

In this paper, we reported the optical process of merocyanine dye LB films by UV spectroscopy, AFM, and QCR method. The electrical behaviors of QCR deposited with dye LB film will be discussed as to the spectroscopic changes of dye LB film under UV irradiation to investigate possible application to optical analysis using QCR. The experimental results show that resonant frequency shift of QCR deposited with dye LB films can be originated by structural change in optical process. And they showed the quantitative relationship between frequency shift and absorption peak, which mean the application possibility of QCR to optical analysis.

Acknowledgments

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