

수정진동자를 이용한 지방산의 고체 증착

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Solid deposition of fatty acids on a quartz crystal resonator

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Introduction

The detection methods for extremely small matters, such as SEM, TEM, AFM, DLS and ICP, have been developed in various scientific and engineering fields, but a real-time detection or in-situ detection is still limited. A quartz crystal resonator comprised a thin quartz crystal sandwiched between two metal electrodes that establishes an alternating electric field across the crystal, causing vibrational motion of the crystal at its resonant frequency. This frequency is sensitive to mass changes at the interface of the sensor [1]. Because the resonator is so sensitive, it can be utilized to determine a phase change in micro-scale near the resonator interface in real-time basis. The crystal formation and growth in a cooling crystallization has been monitored with the quartz crystal resonator to find the beginning moment of the crystallization, to determine a metastable zone width, to measure the hysteresis between the processes of crystallization and dissolution, and to examine the nucleation process of highly supersaturated dilute solution [2].

PVD (Physical Vapor Deposition) is a fine technique to form the crystal phase having good quality from a melt under vacuum, whereas melt crystallization is a mass purification technique for metals and organic compounds. However, it is difficult to measure the deposition rate, i.e., growth rate, of solid phase in the PVD, because the rate is quite low. The cold quartz crystal sensor is a good means for measuring the growth rate of solid phase in the PVD in real time. The separation capacities of the PVD and melt crystallization can be compared if the growth rate of solid phase by the PVD is determined using the quartz crystal sensor.

We proposed a computation formula of the interfacial distribution coefficient [3], and have applied the suggested model to experimental works [4]. The distribution coefficients at a solid interface are essential for the design of the PVD and melt crystallization processes. We have already reported the distribution coefficient of fatty acids during melt crystallization on a rotating cold cylinder, and described that as a function of growth rate using different mass transfer coefficients.

The objectives of this study are to examine whether the cold quartz crystal sensor is a good tool measuring experimentally the amount of solid deposit and to determine the distribution coefficient of fatty acids in PVD in comparison with the distribution coefficient in melt crystallization as a function of growth rate.

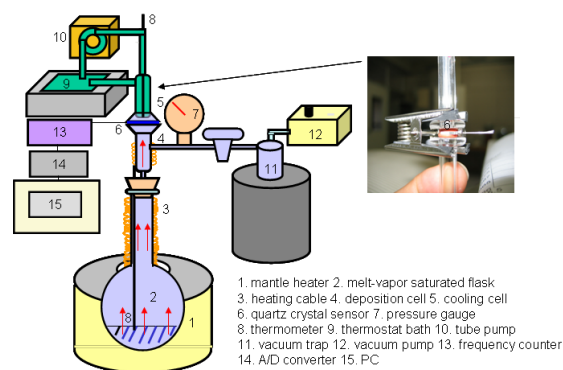


Fig 1. A schematic of experimental apparatus.

Experimental

Material used in this work was a binary fatty acid mixture consisting of lauric acid and myristic acid at a purity of more than 98% purchased from the Kanto Chemical Co., Japan. Figure 1 shows a schematic diagram of the PVD apparatus containing the quartz crystal sensor. The fatty acid vapor was formed from the binary melt in a flask heated up to a certain temperature with a mantle heater. The cold quartz crystal sensor was placed on the top of the flask, and the temperature of the cold sensor, T_c , was kept at a temperature of 288 K using circulating water temperature-controlled with a thermostat. The binary vapor was deposited on the cold quartz crystal sensor after the evacuation pressure, P^{ex} , was maintained at a pressure of 2.5 Pa. The composition of lauric acid in vapor phase, y_L , was fixed at 0.5 by maintaining the composition of lauric acid in melt phase, x_L , at 0.19, according to the VLE (Vapor-Liquid Equilibrium). The x-y relationship of the VLE for lauric acid and myristic acid system does not considerably change with temperature. The operation factor as a driving force of the PVD was the melt temperature, T_m , that directly affects the vapor pressure of melt, P^s . Table 1 lists the experimental conditions in this work.

Table 1 Experimental conditions

No.	T_m [K]	P^s [Pa]	T_c [K]	P^{ex} [Pa]	x_L [-]	y_L [-]
1	353	2.8	288	2.5	0.19	0.5
2	373	12	288	2.5	0.19	0.5
3	398	54	288	2.5	0.19	0.5
4	423	214	288	2.5	0.19	0.5
5	448	726	288	2.5	0.19	0.5
6	473	2180	288	2.5	0.19	0.5

As for the property of quartz crystal sensor, an 8 MHz resonator detects a mass variation of 1.0 ng/Hz found from resonant frequency measurement [5]. The deposition area of fatty acid on the sensor was 0.19 mm². The growth rate of solid phase, V , on the cold quartz crystal sensor was determined from the rate of frequency variation of the sensor, G . The solid deposit of fatty acids was formed on the left side of the cold quartz crystal sensor. The deposit was dissolved in acetone for the composition analysis. A gas chromatograph (Model GC-8A, Shimazu Co., Japan) having an FID detector and a column (Unisole 400, Uniport S 60/80, 3φ, 1 m long, Shimazu Co., Japan) was utilized in the determination of lauric acid composition of the deposit. The analytical error limit of the GC was less than 0.1 %. The distribution coefficient of lauric acid, K_L , was calculated as the ratio of the composition of lauric acid in solid phase, z_L , to the composition in vapor phase, y_L .

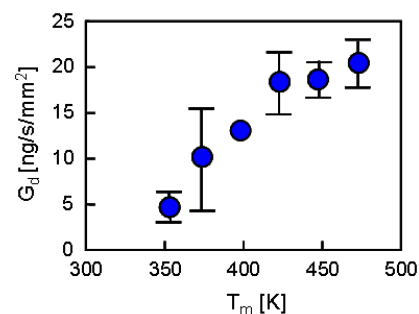


Fig 2. Deposition rate as a function of melt temperature.

Results and Discussion

The temperature of the cold quartz crystal sensor was kept at 288 K. The melt temperature was increased as quickly as possible with a mantle heater, and that was maintained at a certain temperature. The frequency began to decrease when the melt temperature reached to the temperature. The growth rate, V , or deposition rate, G , of the solid phase was determined from the average rate of frequency variation.

3.1 Deposition rate and composition of lauric acid in solid phase

Figure 2 shows the deposition rate as a function of melt temperature. The melt temperature increased the deposition rate proportionally even though the vapor pressure as a driving force of the PVD was exponentially raised with the elevation of melt temperature. It is interesting to represent the deposition rate with the vapor pressure such as

$$G = k[P^s(T_m) - P^{ex}] \quad (1)$$

However, we did not use the above formula, because the deposition rate can be directly obtained from the variation of resonant frequency of a quartz crystal sensor. Figure 3 shows the composition of lauric acid in solid phase as a function of melt temperature. The melt temperature raised the composition of lauric acid, but the composition was unexpectedly small. When we consider the driving force of the PVD from individual components—lauric acid or myristic acid, two driving forces of lauric acid and myristic acid are the same because the composition of lauric acid in vapor phase is equal to that of myristic acid. Probably the vapor-solid equilibrium of lauric acid–myristic acid system has a simple eutectic phase diagram as in the liquid-solid equilibrium of the system. Therefore, pure myristic acid was initially formed in the solid deposit on the surface of a quartz crystal sensor at low melt temperature. As the melt temperature was elevated, however, the deposition occurred under non-equilibrium condition at such a low deposition rate and a small amount of lauric acid was included in the deposit. The increase of lauric acid composition with the rise of melt temperature indicates that the condition on the sensor surface becomes farther from the condition of vapor-solid equilibrium when the melt temperature is raised.

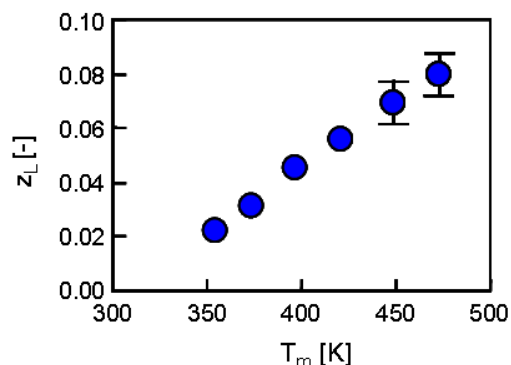


Fig 3. Weight fraction of lauric acid in deposits as a function of melt temperature.

3.2 Distribution coefficient as a function of growth rate

It is obvious that there is a distribution of a component at the vapor-solid interface during the PVD. When the distribution of lauric acid between vapor and solid phases is considered, the distribution coefficient, K_L , is defined as the ratio of the composition of lauric acid in solid phase to the composition in vapor phase.

$$K_L = \frac{Z_L}{Y_L} \quad (2)$$

Also, the growth rate of solid deposit, V , is computed from the deposition rate, G , as follows.

$$V = G / \rho_s \quad (3)$$

where ρ_s is the density of solid phase, 0.9 g/mL. The distribution coefficient should be zero predicted from the eutectic phase diagram of vapor-solid equilibrium as discussed above, but the figure indicates that the experimental outcome was yielded at a non-equilibrium condition. In our previous study [6], a computation equation of the distribution coefficient in melt crystallization was proposed as

$$k_L = 1 - (1 - k_0) \sqrt{\frac{1 - \exp(-V_{min} / k_{m0})}{1 - \exp(-V / k_{m0})}} \quad (4)$$

where k_0 is the equilibrium distribution coefficient and is equal to zero. Therefore, the only correlating parameters are V_{\min} and k_{m0} . The distribution coefficient of a fatty acid during the melt crystallization on a rotating cold cylinder was described as the ratio of the composition in solid to the composition in melt while the coefficient in the PVD was defined as the ratio of solid composition to vapor composition. Note that there is a difference in the definition between the distribution coefficients. Figure 4 depicts two distribution coefficients calculated from the composition of vapor phase in the PVD and from the composition of melt phase in the melt crystallization. It is common that the growth rate in the PVD is lower than that in the melt crystallization, which is demonstrated from the experimental results in the figure. In addition, the distribution coefficient in the PVD was much smaller than that in the melt crystallization. The distribution coefficients computed from the experimental results were correlated using Eq. (4), and the correlation parameters were found as listed in Table 2. Whereas the specific growth rate, V_{\min} , was not much different each other, the mass transfer coefficient, k_{m0} , in the PVD was much larger than that in the melt crystallization. We found that the distribution coefficient in the PVD might be too small to correlate using Eq. (4).

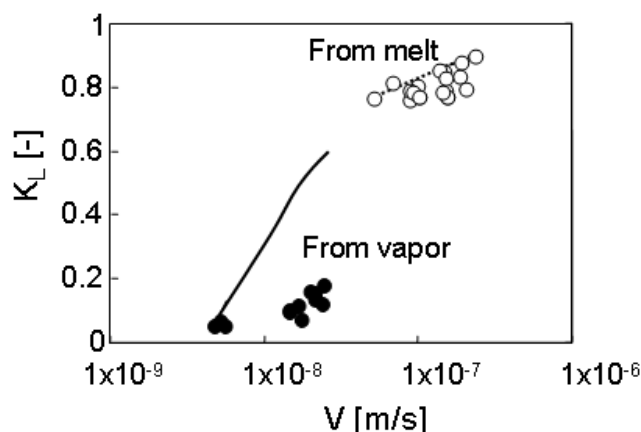


Fig 4. Distribution coefficient of lauric acid as a function of growth rate from melt phase and vapor phase and computed curves from correlation function.

Table 2. Correlation parameters in Eq. (4).

Process	k_{m0} [m/s]	V_{\min} [m/s]
PVD	1.0×10^{-3}	4.5×10^{-9}
Melt crystallization	7.8×10^{-7}	3.0×10^{-9}

Conclusion

The proposed cold quartz crystal sensor detected an extremely small amount of fatty acid deposit from vapor phase in the PVD. The growth rate and the composition of lauric acid in the solid deposit were measured while the melt temperature was varied. The melt temperature was a good operation variable that altered the vapor pressure of the melt as a driving force according to the VLE of lauric acid and myristic acid system. The melt temperature increased the growth rate of solid phase on the sensor surface and the composition of lauric acid in the phase. The distribution coefficient in the PVD was correlated as a function of growth rate and so be the distribution coefficient in the melt crystallization. It was found that the distribution coefficient in the PVD was much smaller than that in the melt crystallization.

Acknowledgments

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