Ultrathin-film differential-thermal-analysis apparatus with simultaneous photoemission measurements

Yasushi Yamamoto, Toshiaki Enami, Masakazu Kuroi, Noritaka Matsuie, and Hisao Ishii
Department of Chemistry, Graduate School of Science, Nagoya University, Nagoya 464-8602, Japan

Kazuhiko Seki
Department of Chemistry, Graduate School of Science and Research Center for Materials Science, Nagoya University, Nagoya 464-8602, Japan

Yukio Ouchi[a)]
Department of Chemistry, Graduate School of Science, Nagoya University, Nagoya 464-8602, Japan

We developed an apparatus of differential thermal analysis (DTA) capable of simultaneous surface specific ultraviolet (UV) photoemission measurements to investigate thin-film phase transitions. The apparatus was installed in a vacuum chamber of 10^{-6} Torr range for thermal isolation and the measurements of UV photoemission. As a sample substrate, we used a thin (10 μm) copper sheet supported by two wires for optimal thermal resistivity. The performance of the apparatus was examined using a 650-Å-thick pentacontane (n-$C_{50}H_{102}$) film, which may exhibit a unique monolayer phase transition known as surface freezing. We observed two anomalies of DTA curve around the bulk melting temperature, one of which is apparently due to the bulk melting. Since the temperature dependence of the surface specific UV photoemission measurements showed corresponding changes in photoemission current, we could conclude that the other phase transition peak originates from the surface freezing effect. This demonstrates that our DTA-UV apparatus is sufficiently sensitive to examine such monolayer phase transitions. © *2000 American Institute of Physics.* [S0034-6748(00)05103-0]

I. INTRODUCTION

Since the discovery of the surface freezing effect of n-alkanes,[1] this effect has been the subject of recent interest.[2,3] The surface freezing refers to the phenomenon that a thin layer at an air/liquid interface crystallizes at a higher temperature than that of the bulk freezing while cooling a liquid substance. The bulk part of an n-alkane, in other words, melts first on heating, and the thin layer at the surface melts at a slightly higher temperature. This is contrary to the general surface-melting behavior observed in other crystals.[4] We have studied the surface freezing effect of long-chain alkanes with use of near edge x-ray absorption fine structure (NEXAFS) spectroscopy[5,6] and determined the molecular orientation angle in the frozen surface layer from the polarization dependence of the observed spectra. The spectra were obtained by a total-electron yield mode, where data are taken as the number of photoelectrons emitted per incoming photon as a function of photon energy. The measurement possesses a surface sensitivity of several nanometers because of the short escape depth of photoelectrons.[7]

The structure of the thin frozen surface layer of n-alkane has been systematically studied by the grazing incidence x-ray diffraction technique.[2,3,8] It has been revealed that the thin layer consists of a molecular monolayer with a quasi-long range crystal structure and that the transition from an isotropic liquid phase is of the first order. The molecular long axis is parallel to the surface normal for alkanes with the carbon number less than 30, while it is tilted for the longer alkanes. The carbon number of alkyl chains which exhibit surface freezing ranges from 16 to 50. Several other techniques such as ellipsometry[9] and infrared-visible sum-frequency generation spectroscopy[10] have been applied to the surface freezing phenomena to support the above findings. Reflection microscopic measurements have also been used to study a wetting transition of alkanes on oxidized Si substrates, which may be related to the surface freezing behavior.[11] Theoretical works have also been performed on the basis of longitudinal fluctuations[12] and of lattice-gas models.[13]

For obtaining further insight, it is important to examine this effect from a thermodynamic viewpoint. Although many studies of thermal analysis have been performed to investigate thin layers adsorbed on solids, most of them used powder solid specimen to gain large surface area, and only few apparatuses have been reported for the studies of flat thin films. For example, Geer *et al.* have developed an ac calorimeter for thin films and performed the heat capacity measurements of free-standing liquid-crystal films.[14] Nomaki *et al.* have performed the differential scanning calorimetry (DSC) measurement of Cd–stearate Langmuir–Blodgett films.[15] For examining the surface freezing effect, we also need to construct a thermal analysis apparatus having a similar potential to observe monolayer phase transitions of a film form.

[a)]Author to whom correspondence should be addressed; electronic mail: ouchi@mat.chem.nagoya-u.ac.jp

1788

Surface sensitive measurement such as NEXAFS or other photoemission techniques may help our thermal analysis of the surface freezing effect. This is because an interface-related phase transition (wetting or dewetting) may occur not only at an air/liquid or vacuum/liquid interface but also a liquid/substrate interface. When we observe any thermal anomaly, we should examine at which interface the thermodynamic change occurs. If we detect a corresponding anomaly in surface sensitive photoemission, we can safely ascribe the transition to the air/liquid (or vacuum/liquid) interface. At the same time, however, the combination of thermal analysis with surface sensitive photoemission techniques also sets same boundary conditions when constructing the apparatus. For example, the NEXAFS technieque requires us to use a flat sample and also to set a substrate vertically in a high-vacuum chamber to match the experimental condition of the incidence of horizontally polarized soft x-ray synchrotron radiation. Furthermore, the apparatus should be as simple as possible not to electronically interfere with photoemission measurements.

In this article, we will report a design and construction of such a thermal analysis apparatus capable of simultaneous detection of the structural change at the surface region by the photoemission techniques. As for the thermal analysis method, we have adopted the differential thermal analysis (DTA) technique. This is because DTA is a simple and direct method, which monitors the temperature difference ΔT between the sample and the reference. Since we are interested in detecting the surface freezing effect, the thermal analysis unit should possess a high sensitivity and DTA may have such a potential. Another advantage of DTA is that we can roughly determine the temperature and the enthalpy of the phase transition. Using an appropriate material for calibration, transition enthalpy of the first order phase transition can be obtained.

Although this apparatus is compatible with NEXAFS measurements, for the first test of performance for detecting the surface structural change in the laboratory, we used a rather simple ultraviolet (UV) photoemission technique.[16] The escape depth of UV photoelectrons is short (<50 Å),[7] providing an appropriate surface sensitivity for detecting the surface freezing transition. The surface freezing effect of n-alkane could be successfully confirmed with simultaneous use of these two methods.

II. DESIGN AND CONSTRUCTION OF DTA-UV PHOTOEMISSION APPARATUS

A. DTA part

In Fig. 1, we show the main part of our DTA apparatus. The substrate part is illustrated in Fig. 1(a). The sample substrate (SS) and the reference substrate (RS) are formed by making a rectangular hole of 8×20 mm^2 at the center of a copper sheet of 20×26 mm^2 with 10 μm thickness. Two pieces of copper wires of 0.3 mm diameter are soldered using a small amount of solder (at 6.5 mg) along the shorter ends of the copper sheet at a distance of 1.5 mm from the ends to support the sheet and to supply heat from a ceramic heater H (ADAMANT $10 \times 30 \times 1$ mm^3, 100 V 30 W) in Fig.
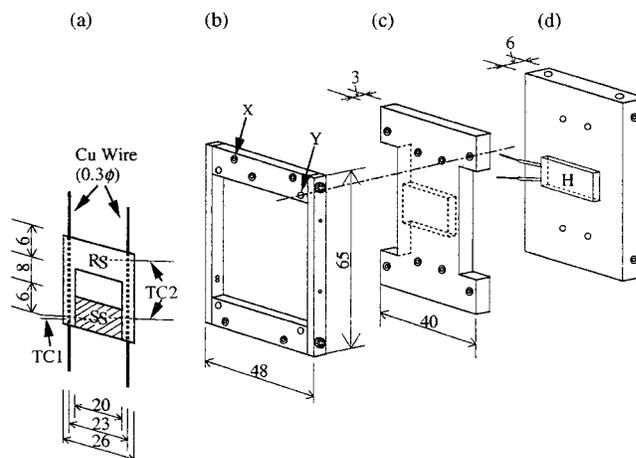

FIG. 1. DTA apparatus: (a) substrate part; SS: the area for sample deposition, RS: reference area, TC1: chromel–alumel thermocouple for sample temperature measurement, TC2: constantan wires for forming thermocouples for temperature difference ΔT measurement, (b)–(d) other parts of DTA unit; (b) stainless steel holder, X: the screw holes for fixing (a), Y: the screw holes for fixing (b)–(c), (c), and (d) heater block; H: ceramic heater (in mm).

1(d). The temperature difference ΔT between SS and RS was measured with two constantan wires of 0.1 mm diameter fixed at the center of the SS and the RS by 0.3 mg of solder, respectively. Here the copper substrate works as one of the components of copper–constantan thermocouples. The sample temperature was detected with a chromel–alumel thermocouple of 0.1 mm diameter fixed by epoxy resin at the center of the SS. We tried various combinations of materials, substrate thicknesses, and the diameters of wires, and obtained the optimum results with a sufficiently good sensitivity, for observing the phase transition of a monolayer by the above-mentioned values. Figures 1(b)–1(d) illustrate other parts of the DTA unit. The copper wires soldered onto the DTA substrate [Fig. 1(a)] are fixed by screws at the holes marked X to a stainless steel holder of 65×48 mm^2. The distances from the screw to the RS and the SS are kept the same. The stainless steel holder is mounted onto a heater block of $65 \times 40 \times 9$ mm^3 [Figs. 1(c) and 1(d)] formed by two copper plates, where H is sandwiched. The heat flow mostly goes through the two copper wires to the sample part under vacuum of 10^{-6} Torr as described in Sec. II C. Figure 2 schematically illustrates how the DTA unit is connected to the manipulator of the vacuum chamber. The unit shown in Fig. 1 is mounted on a stainless steel block and then fixed to the manipulator rotatable around a vertical axis for measurements of the incident angle dependence of the NEXAFS spectra using synchrotron radiation. We electrically insulated the whole DTA unit from the manipulator by inserting a poly(tetrafluoroethylene) disk, and a copper wire L of 0.25 mm diameter is connected to the substrate. The photoelectron emission by the irradiation of UV light was monitored as a drain current from the substrate to the wire.

B. UV Light source for photoemission

The UV photoemission light source is illustrated in Fig. 3. We used a He discharge lamp which emits He I(21.2 eV) resonance line. The He discharge lamp consists of two stain-
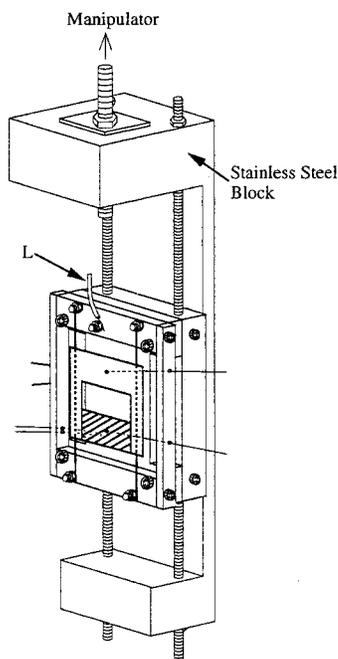
FIG. 2. Setup of the DTA unit for the manipulator; L: copper wire for drain current monitor.

less steel electrodes separated by a poly(tetrafluoroethylene) disk and a quartz pipe (i.d. 1 mm, 30 mm length) where the discharge occurs. The cathode and anode were cooled by water circulation and a cooing fan, respectively. The discharge condition can be roughly monitored by looking at the color of the discharge through a closed glass pipe at the right end of Fig. 3. UV light impinges upon the sample through a differential pumping part, where He gas after discharge is pumped away with a rotary pump of 2 ℓ/s. Typical voltage and current for discharge were 400 V and 20 mA supplied by a homemade dc power supply through a ballast resister of 10 kΩ and 200 W, and the He pressure was 1.1 Torr. The spot size of the ultraviolet light was 5 mm diameter on the substrate as monitored by irradiating to the copper substrate. The electrical signals were taken out through BNC connectors via shielded cables.
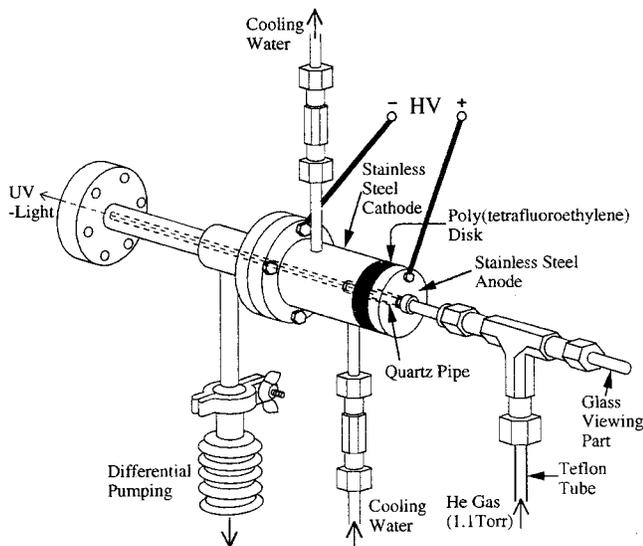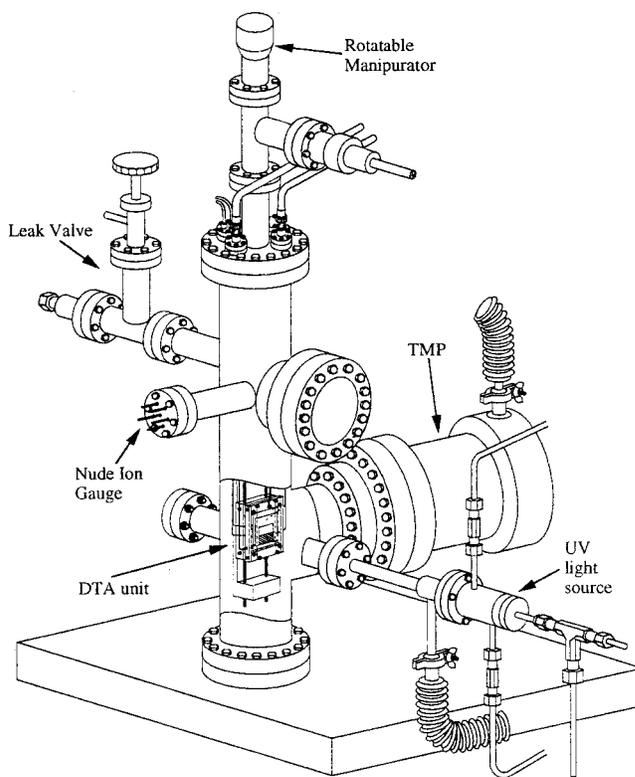

FIG. 3. UV light source.

FIG. 4. The whole set up of the DTA-UV photoemission measurement apparatus.

C. Setup of the apparatus

In Fig. 4, we present the whole setup of the DTA-UV photoemission apparatus. The vacuum chamber is evacuated by a turbomolecular pump of 480 ℓ/s (SEIKO SEIKI, α451) to a vacuum of 10^{-6} Torr range.

Figure 5 shows the connection diagram of the electric apparatuses. The ceramic heater is connected to a regulated dc power supply (Kikusui Electronics, PAD110-5L). The thermocouple (TC1) monitors the sample temperature with a digital multimeter (Advantest, TR6847). The standard temperature of 0 °C was obtained using a mixture of crushed ice and water. The two constantan wires (TC2) from the DTA substrate are lead to a nanovoltmeter (Hewlett–Packard, HP34420A). The nanovoltmeter and digital multimeter are controlled by a personal computer (NEC PC9801 RX). The copper wire L used for the drain current measurement is connected to a picoammeter (Takeda Riken, TR8641) and its
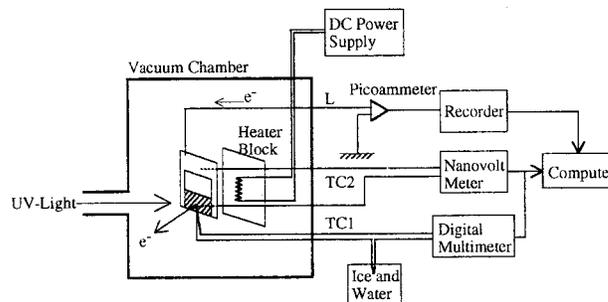

FIG. 5. Connection diagram of the electric apparatuses. TC1: chromel–alumel thermocouple for sample temperature measurement, TC2: constantan wires for forming thermocouples for temperature difference ΔT measurement, L: copper wire for drain current monitor.
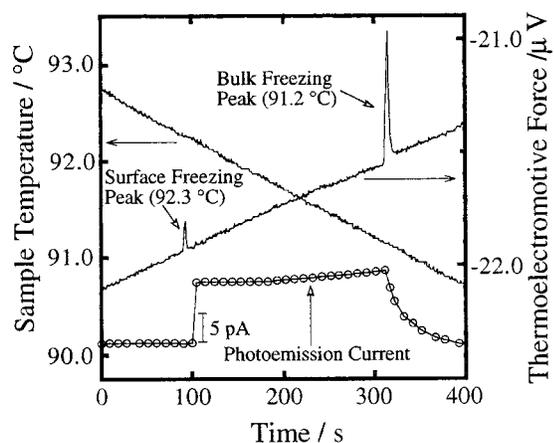
FIG. 6. DTA curve and change in photoemission current of a pentacontane film at the cooling process from the isotropic liquid phase.

output is fed to a recorder (Rikendenshi D-72BP) and to the computer.

III. SURFACE FREEZING OF n-$C_{50}H_{102}$

For examining the performance of the present apparatus, we studied the surface freezing of a long-chain n-alkane pentacontane (PC:n-$C_{50}H_{102}$). Before actually examining surface freezing, we carried out several preparatory experiments. At first, we measured the melting point T_m of a bulk sample with a DSC (Seiko Denshi, DSC120U) and obtained T_m as 91.2 °C. Then we performed DTA measurements for a bulk sample (0.1 mg) of PC. To calibrate the temperature of our DTA system, we visually confirmed the melting and regarded the onset temperature of the observed DTA peak as the melting point.[17]

The thin film specimen was prepared as an evaporated film of 650 Å in thickness on the sample area SS of the copper substrate as shown in Fig. 1. The evaporation was carried out in a separated evaporation chamber at a vacuum of 10^{-5} Torr, and the film thickness was monitored with a quartz oscillator, and the rate of evaporation was 10 Å/min. DTA and photoemission measurements were performed simultaneously around the temperature range of the melting point observed for the bulk PC sample (0.1 mg). The increasing and decreasing rate of temperature was 0.4 and 0.3 °C/min, respectively. The melting point of the bulk part of the evaporated PC film agreed well (within 0.1 °C) with the bulk melting point, as described later.

In Fig. 6, we show a typical set of the DTA curve and the variation in photoemission current of PC at the vicinity of the bulk freezing point at the cooling process from an isotropic liquid phase. The photoemission current is shown in arbitrary units. We observed two anomalies at 92.3 and 91.2 °C, where stepwise increase and decrease of the photoemission current were also detected. As mentioned above, the larger peak at 91.2 °C is due to the bulk freezing transition. Considering the surface specificity of UV photoemission,[16] we can attribute the first small peak at 92.3 °C to the surface freezing at the air/liquid interface rather than the transition at the liquid/substrate interface. At the heating process, we could also detect the corresponding phenomena; after the bulk melting peak we observed a small

(and broader) peak which is attributable to the melting of the surface layer. The present DTA curve does not show a separate third peak corresponding to the freezing at the PC/substrate interface. Although it is difficult to deduce the transition order of the surface freezing effect, it has been discussed experimentally and theoretically.[2,3,5,6,8,9,12,13,18] Studies by surface tension,[2,3,8] ellipsometry,[9] and NEXAFS[5,6] measurements concluded that it is a first-order transition. Finally we should refer to the sensitivity of our DTA apparatus. The peak height observed for the surface freezing of PC was 125.3 nV from the baseline, while a typical noise level of our DTA signal was ±4.1 nV. Thus this instrument should be able to detect even weaker peaks than those examined in the present study.

IV. DEPENDENCE ON THE PRESSURE OF AMBIENT GAS

The present DTA apparatus is used in high vacuum for simultaneous NEXAFS or UV photoemission measurements, where vacuum is necessary for its electron yield detection.[7] In terms of the thermal analytical condition, the high vacuum chamber also provides an ideal thermal insulation around the sample/reference materials. This is because the heat transferred from the two copper wires are at least 10^6 order of magnitude lager than those by a thermal radiation effect or by a direct thermal conduction of 10^{-6} Torr atmosphere.[19] Thus it is quite understandable that our apparatus does not require a well-designed and symmetric thermal jacket even though it is applicable to detect a monolayer phase transition. At the same time, however, this high vacuum limits the length of alkanes toward the shorter direction because of the sublimation of the specimen with high vapor pressure. If we can use the apparatus under ambient gas, the sublimation may be suppressed due to the slow diffusion of the evaporated alkane molecules. Thus, we examined how high vacuum is required in order to monitor the surface freezing effect. Under low vacuum condition, thermal conduction and convection flow of the gas may affect the reliability of the analysis.

Figure 7 shows the DTA curves of PC taken at several vacuum pressures realized by introducing a small amount of N_2 through a leak valve: (a) low vacuum (LV) 1.2×10^{-1} Torr, (b) medium vacuum (MV) 1.3×10^{-3} Torr, and (c) high vacuum (HV) 2.7×10^{-7} Torr in the cooling process without conducting photoemission measurement. Temperature decreasing rates are: (a) 0.34 °C/min, (b) 0.28 °C/min, and (c) 0.25 °C/min, respectively. We observed the anomalies related to the surface freezing transition for HV, MV, and LV as well as the peaks of the bulk freezing transition. It is noticeable that the anomalies of the surface freezing for HV and MV cases are observed as peaks; but that for LV appears as a stepwise discontinuous change of the DTA curve. The profile difference of the DTA curve for LV strongly suggests that the thermal environment was drastically different from those for MV and HV. Actually, it is known that the atmosphere behaves like a gas–fluid so that convection heat transfer may not be negligible when the mean free path $\Delta \ell$ of N_2 molecules becomes smaller than
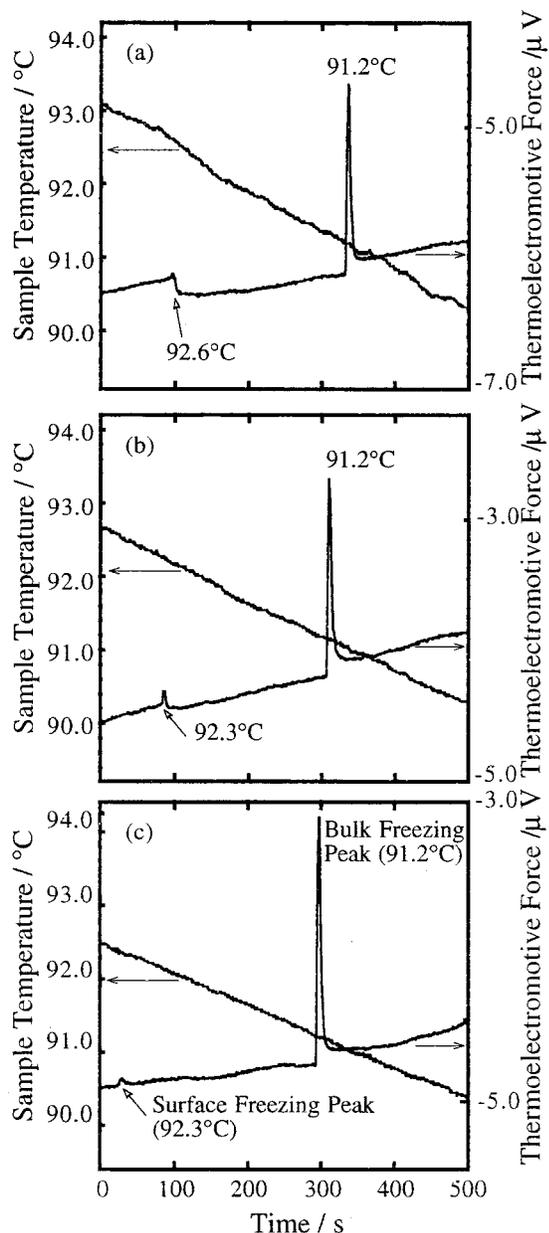
FIG. 7. Dependence of DTA measurement on ambient pressure: (a) 1.2 $\times 10^{-1}$ Torr, (b) 1.3×10^{-3} Torr, and (c) 2.7×10^{-7} Torr.

V. DISCUSSION

We have developed an apparatus of DTA capable of the simultaneous measurements of surface specific UV photoemission to investigate a thin-film phase transition in a vacuum chamber. The vacuum necessary for a reliable measurement was found to be 10^{-3} Torr or better. In a preliminary experiment on the analysis of the surface freezing effect of a pentacontane (n-$C_{50}H_{102}$:650 Å) film, we could successfully observe an additional transition anomaly in a DTA curve besides the bulk transition. Since the surface specific UV photoemission measurement exhibited a corresponding change in its emission intensity, we could conclude that the anomaly is due to the surface freezing. Our DTA apparatus with a low noise level of ± 4.1 nV can be applied to investigate various phase transitions observed in other systems such as polymer films, self-assembled monolayers, and liquid crystals.

ACKNOWLEDGMENTS

the typical dimension of the apparatus.[19,20] $\Delta\ell$ of N_2 molecules at 10^{-2} Torr is approximately 1 cm,[19] which is comparable to a typical distance of the heater and the sample. The larger fluctuation of the sample temperature shown in Fig. 7(a) may be caused by the thermal convection effect.[20] Furthermore, the surface freezing transition was observed at a 0.3 °C higher temperature than that of the HV case. This should be also due to the fact that a nonnegligible amount of the heat flowed from the top surface to the atmosphere and hence the local temperature of the surface freezing layer was 0.3 °C lower than that of the substrate.[19] This non-negligible heat transfer may also explain the stepwise discontinuous change of the DTA curve in terms of the change of thermal resistivity between the sample and the atmosphere. From the results of Fig. 7, we can conclude that our DTA chamber requires a vacuum of 1.0×10^{-3} Torr or better.

[1] D. M. Small, *The Physical Chemistry of Lipids* (Plenum, New York, 1986).
[2] X. Z. Wu, B. M. Ocko, E. B. Sirota, S. K. Sinha, M. Deutsch, B. H. Cao, and M. W. Kim, Science **261**, 1018 (1993).
[3] X. Z. Wu, B. M. Ocko, E. B. Sirota, S. K. Sinha, and M. Deutsch, Physica A **200**, 751 (1993).
[4] D.-m. Zhu and J. G. Dash, Phys. Rev. Lett. **57**, 2959 (1986).
[5] Y. Yamamoto, R. Mitsumoto, T. Araki, Y. Ouchi, K. Seki, and Y. Takanishi, J. Electron Spectrosc. Relat. Phenom. **78**, 367 (1996).
[6] Y. Yamamoto, R. Mitsumoto, T. Araki, Y. Ouchi, K. Seki, N. Ueno, and Y. Takanishi, J. Phys. IV **7**, C2-709 (1997).
[7] J. Stöhr, *NEXAFS Spectroscopy* (Springer, Berlin, 1992).
[8] B. M. Ocko, X. Z. Wu, E. B. Sirota, S. K. Sinha, O. Gang, and M. Deutsch, Phys. Rev. E **55**, 3164 (1997).
[9] T. Pfohl, D. Beaglehole, and H. Riegler, Chem. Phys. Lett. **260**, 82 (1996).
[10] G. A. Sefler, Q. Du, P. B. Miranda, and Y. R. Shen, Chem. Phys. Lett. **235**, 347 (1995).
[11] C. Merkel, T. Pfohl, and H. Riegler, Phys. Rev. Lett. **79**, 4625 (1997).
[12] A. V. Tkachenco and Y. Rabin, Phys. Rev. Lett. **76**, 2527 (1996).
[13] F. A. M. Leermakers and M. A. C. Stuart, Phys. Rev. Lett. **76**, 82 (1996).
[14] R. Geer, T. Stoebe, T. Pitchford, and C. C. Huang, Rev. Sci. Instrum. **62**, 415 (1991).
[15] T. Nomaki, A. Yamanaka, and K. Naito, Anal. Sci. **7**, 1287 (Supplement 1991).
[16] S. Hüfner, *Photoelectron Spectroscopy* (Springer, Berlin, 1995).
[17] G. Lombardi, *For Better Thermal Analysis*, 2nd ed. (ICTA, Rome, 1980).
[18] Y. Yamamoto, H. Ohara, K. Kajikawa, H. Ishii, N. Ueno, K. Seki, and Y. Ouchi, Chem. Phys. Lett. **304**, 231 (1999).
[19] J. P. Holman, *Heat Transfer* (McGraw-Hill, New York, 1976).
[20] P. W. Atkins, *Physical Chemistry*, 5th ed. (Oxford University Press, Oxford, 1992).