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Interaction between surface migrating pentacene molecules and chemically modified surfaces of silicon oxides studied by pulsed molecular beam scattering

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Abstract

The interaction between pentacene molecules and organic self-assembling monolayers formed on silicon oxides (SiO_2) was studied by measuring the surface scattering time profile of the pulsed molecular beam of pentacene. It was found that the surface residence time (SRT) of pentacene was significantly reduced on a surface treated with hexamethyl silazarane (HMDS) compared with that on a bare SiO_2 surface. The activation energies derived from the temperature dependence of the SRT were 24 kJ/mol and 100 kJ/mol for HMDS–SiO_2 and the bare SiO_2, respectively. A surface treated with octadecyltrichlorosilane (OTS) showed SRT values almost the same as those on the bare SiO_2 surface, which was due to exposed SiO_2 regions on the thermally-degraded OTS–SiO_2. The growth mechanism with improved quality is due to the shallower adsorption potential and enhanced migration of pentacene by the surface alkylation.
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Growing thin films with large grain sizes is of particular importance to improve the performance of organic thin film devices. The grain size is governed by the nucleation density in the initial growth processes and surface migration plays essential roles in it. Although it was recently reported that chemical modification of the substrate surfaces drastically improves the device performance of field effect transistors made of pentacene [1,2] the precise mechanism for the improved interface formation has not been clarified. It is not understood how to determine the optimum chemical group for the best device fabrication.

There are various techniques to study the interaction between molecules and surfaces, but most of them are not applicable to study the thin film growth of organic semiconductors. Thermal desorption spectroscopy of monolayer adsorbates is difficult because the heating of monolayer adsorbates makes molecules aggregate on the surface and the cohesive energy of the organic films can only be obtained [3]. Contact angle measurement of various liquids on the surface will reveal the interaction between functional groups and the surfaces, but the information is macroscopic and indirect. In contrast, pulsed molecular beam scattering is a powerful technique to elucidate the interaction between the molecules and the surfaces. This technique has been applied to inorganic thin film growth [4–6] and molecular film formation on inorganic surfaces [7,8]. In this paper, we report the pulsed molecular beam scattering of pentacene by the chemically modified surfaces of SiO_2.

A schematic drawing of the pulsed molecular beam scattering apparatus is shown in Fig. 1 [7]. The molecular beam of pentacene from a Knudsen-cell is chopped by a rotating chopper and shaped into pulses with a duty ratio of 1/25. Pentacene was evaporated as purchased (Aldrich) and heated to ∼180 °C for the evaporation. The molecular beam was collimated by a slit and scattered by a heated sample
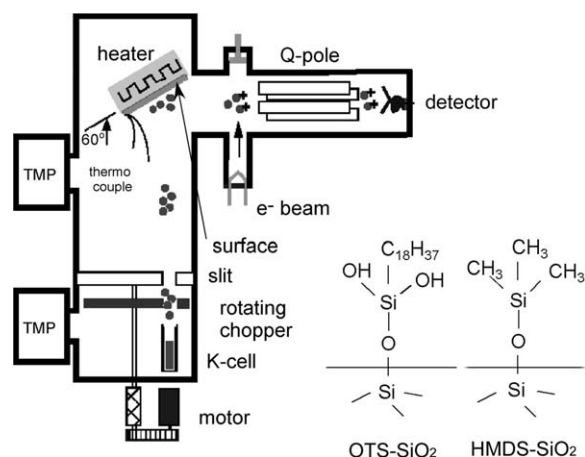
Fig. 1. Experimental setup and the model structures of the chemically modified SiO₂ surfaces.
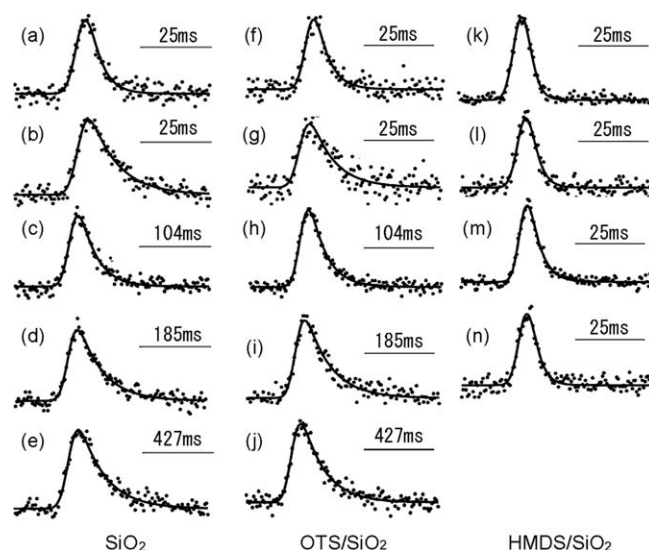

Fig. 2. Time profiles of the intensity of the scattered molecules at various temperatures. The surface materials are indicated below each column. The substrate temperatures are (a) 120 °C, (b) 110 °C, (c) 100 °C, (d) 90 °C, (e) 80 °C, (f) 123 °C, (g) 112 °C, (h) 102 °C, (i) 92 °C, (j) 81 °C, (k) 125 °C, (l) 117 °C, (m) 95 °C and (n) 82 °C.

surface of 55×40 mm². The surface temperature was monitored by six thermocouples in order to ensure good uniformity. The temperature uniformity on the surface was better than ± 10 °C. The scattered molecules are ionized by an electron beam after flying 45 cm. The molecular ions are selected by a quardupole mass filter in order to detect ions having $m/z \geqslant 200$. An electron multiplier (Murata MS-1081B) was used as the ion detector in the pulse counting mode. The time profile was accumulated for about one hour. The time profile was least square fitted by a convolution of the geometrical apparatus function and exponential decay. A "surface residence time" (SRT) was obtained as the reciprocal of the exponential decay constant at each temperature.

The sample surfaces were prepared as follows. The chemical modification of SiO₂/Si was performed according to the literature. A Si(1 0 0) wafer was cut and treated by boiling HCl:H₂O₂:H₂O = 1:1:4 solution, and cleaned by repeatedly immersing it in 1% HF (1 min) and in boiling conc. HNO₃ (10 min). Three types of surfaces were prepared after the final boiling in HNO₃. One is a bare oxide surface obtained just by rinsing the sample in pure water. The second one is OTS-terminated SiO₂ that was obtained by immersing the sample in an OTS solution (2 mM in mixed solution of hexadecane and CCl₄ (1:4)) [9]. The third one is an HMDS treated one which was obtained by refluxing the bare oxide surface in HMDS solution in hexane [10]. All the surfaces were blow dried by dry nitrogen gas and then quickly loaded in the vacuum chamber. The measurement was performed after the baking-out the vacuum chamber at 150 °C and the surface contamination was avoided by heating the sample to slightly higher than the baking temperature. An AFM under ambient conditions was used to characterize the surfaces. The model structures of the chemically modified surfaces are shown in Fig. 1.

Fig. 2 shows the time profile of the pentacene flux scattered by the bare and chemically modified SiO₂ surfaces at various temperatures. The dots and curves are data points from the measurement and the fitting by convolution of the

apparatus function of the rotating slit and exponential decay. The abscissas correspond to the rotation angle (0–360°) of the chopper, which can be converted to the dimension of time. The rotating speed was chosen to obtain the tailing appropriate for the fitting as long as it is lower than the maximum value (500 rpm). The time scales are indicated in each figure. It was noted that the peaks in the measurement of the fastest rotation (shown with "25 ms" scales) are delayed from those with a slower rotation. It can be explained by the flight time of the molecule from the rotating chopper to the detector and it is used as an adjustable parameter in the fitting. The velocity of the molecules estimated from the delay is 210 ± 60 m/s when the substrate temperature is higher than 110 °C, which is almost consistent with the thermal velocity [11] of the flying molecules at the source or substrate temperatures. Additional slowing of the scattered molecules is noticed at lower substrate temperatures, but its effect is negligible on the SRT values when sufficient tailing is observed in the time profile.

Fig. 2 indicates that the characteristic decay time becomes shorter when the substrate temperature is higher. It can be understood by the thermally activated desorption of the surface migrating pentacene. It is also noted that the time profile of the molecules scattered by HMDS–SiO₂ is much shorter than that by bare SiO₂, whereas OTS–SiO₂ shows a behavior similar to that of bare SiO₂. From the fitting, the SRT has been obtained as the exponential decay time constant for each curve. Fig. 3 shows the Arrhenius-type plots of SRT versus inverse temperature. The activation energies for the SRT were 104 kJ/mol, 96 kJ/mol and 24 kJ/mol for the bare SiO₂, OTS–SiO₂ and HMDS–SiO₂, respectively. The error was estimated to be less than