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ANISOTROPIC CRYSTAL GROWTH OF TTF-TCNQ FILMS ON ALKALI HALIDES

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Abstract We probed the mean diffusion length and the growth rate of length, width and height of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) on three kinds of alkali halide substrates, NaCl, KBr and KCl, by means of atomic force microscopy (AFM). The diffusion length is up to the substrates. The growth rate of height for TTF-TCNQ on KCl is much smaller than those on NaCl and KBr. Monte Carlo simulation well explains the experimental results qualitatively.

INTRODUCTION

In order to apply organic thin films to electronics and optical devices it is essential to develop the techniques to control molecular arrangements.[1] Thus it is important to clarify nucleation and growth mechanisms of the organic films. Atomic force microscopy (AFM)[2] is a powerful method for these purposes because it possess the capability to image the surface structures of the films from nanometers to microns regardless of their conductivity. On the other hand, Monte Carlo simulation has been applied for the nucleation and growth mainly of metals and semiconductors, and few studies by the simulation have been reported for organic materials.[3] However, the simulation for organic films also should be very helpful to clarify the crystal growth mechanism.

Tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) is a charge transfer complex consisting of TTF as an electron donor and TCNQ as an electron accepter. The crystal is monoclinic with lattice constants of a = 1.2298 nm, b = 0.3819 nm, c = 1.8468 nm and β = 104.46°.[4] It possess high one-dimensional electronic conductivity along the b-axis, in which each molecule forms a homologous molecular column. TTF-TCNQ is a suitable system at a first step for studying the nucleation and growth mechanism of organic films because the structural and physical properties of bulk crystal have been investigated in detail.[5] It is known to grow epitaxially on the surface of alkali halides with its ab-plane parallel to the substrates.[6,7]

In this study we applied AFM to study the anisotropic crystal growth of TTF-TCNQ deposited on three kinds of alkali halides, NaCl, KBr and KCl, quantitatively. In

order to investigate the crystal growth of TTF-TCNQ, we performed Monte Carlo simulation.

EXPERIMENTAL

The complex was precipitated by mixing two solutions of TTF and TCNQ in acetonitrile. The dried sample was charged in a quartz crucible and sublimated at the temperature of 100 °C and deposited on the substrates, NaCl, KCl and KBr, which had previously been air-cleaved and annealed at 200 °C for 2 hours in a pressure of 1 x 10^{-4} Pa. The substrates were set within 1.6 ° of solid angles from the crucible and the differences of the impinging molecular intensities between the substrates are less than 0.1 %. The temperature of the substrate was kept at 20 °C and in 3 x 10^{-4} Pa during deposition. AFM observation was performed in air at room temperature by use of NanoScope II (Digital Instruments, Inc., Santa Barabara, CA).

RESULTS AND DISCUSSION

First we estimate the incident molecular fluxes to the substrates. The evaporation rate of TTF-TCNQ as a function of the temperature was obtained using the thermogravimetry.[8] By the report it is around 5 x 10^{20} [molecules/m^2·s] at 100 °C. The incident molecular flux to substrate is estimated to be R = ~ 10^{18} [molecules/m^2·s], corrected by Clausing's factor of crucible and the $1/R^2$ distance correction factor (R : the distance between the aperture of the crucible and the substrate).[9]

Figures 1(a) and (b) show typical AFM images of TTF-TCNQ films deposited on NaCl, KBr and KCl substrates for 60 and 300 seconds, respectively. The size of these images is 13.4 μm x 13.4 μm. All films consist of islands with their longer sides parallel to the two equivalent <110> directions of the (001) surface of these substrates. This epitaxial growth has been understood to initiate from the adsorption of two CN groups of TCNQ molecule on cations in the substrate surface at the initial stage.[6,7]

The density of islands on the NaCl is the highest of the three substrates. It becomes saturated after some period of the deposition time. For example, for NaCl substrates, it was around 90 seconds, indicating that arrived molecules on the substrate after 90 seconds do not form a new nuclei, but diffuse on the surface to be captured in the pre-existing islands or desorbed into the vacuum. On the other hand, for the KBr and

KCl substrates, it was confirmed to be around the period of 300 seconds. The saturated densities were 2.8/μm^2,

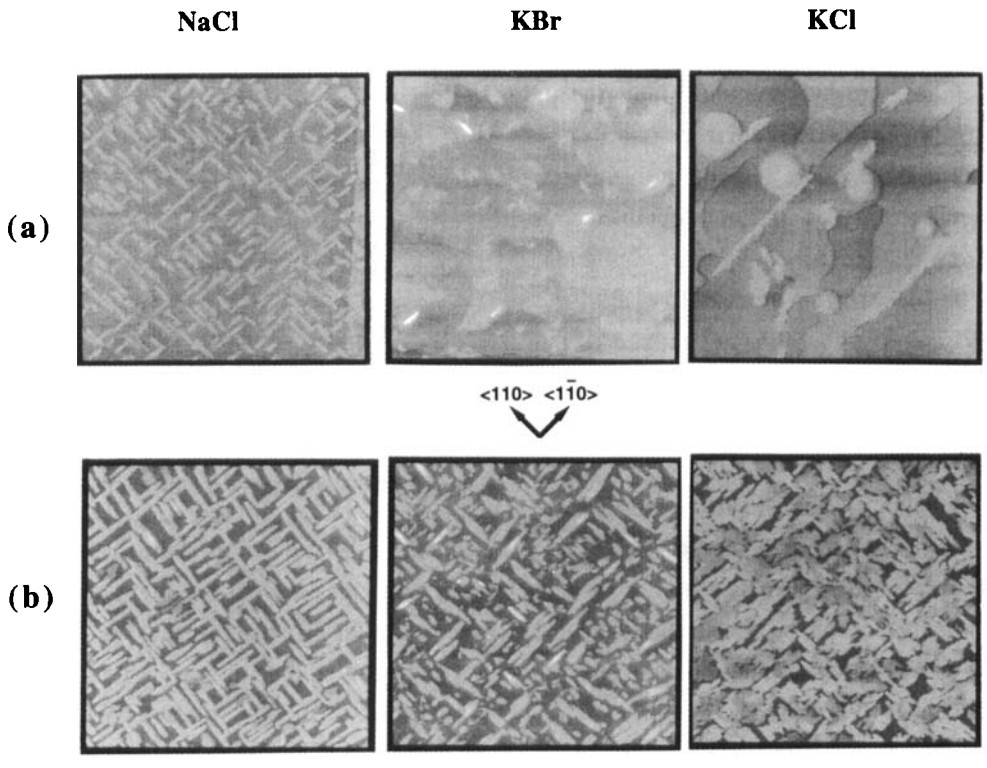

FIGURE 1 AFM images (13.4μm x 13.4μm) of TTF films deposited for (a)60 and (b)300 seconds. See Color Plate III.

1.4/μm^2 and 1.0/μm^2 for the NaCl, KBr and KCl substrates, respectively. The inverse of square root of the saturated density of islands corresponds to the surface mean diffusion length of molecules.[10] They were estimated to be 0.6μm, 0.9μm and 1.0μm for the NaCl, KBr and KCl substrates, respectively.

In order to investigate the crystal growth of TTF-TCNQ on a microscopic scale, the deposition process was simulated by use of Monte Carlo method. Since the details of simulation is beyond the aim of this paper, it is detailed in a separated paper.[11] Figure 2 shows a typical result in the case of a desorption probability and a diffusion probability, 0 and 0.2, respectively. The saturation of the density of islands, as confirmed in the experiments, is reproduced around 2300 loops. Mean length for surface diffusion, λ, of

molecules are related to activation energies of adsorption, E_{ad}, and diffusion, E_d, as follows;[12]

$$\lambda = \frac{a}{2}\exp\left\{\frac{(E_{ad} - E_d)}{2kT}\right\} \quad (1)$$

Where a is a lattice constant, k is Boltzman constant and T is a substrate temperature. Since mean length for surface diffusion corresponds to the inverse of square root of the saturated density of islands, it can be obtained both from the experiment and the simulation. The desorption probability and the diffusion probability are related to the activation energies of adsorption and diffusion. The dependence of λ on E_{ad} and E_d can be reproduced by the simulation. Therefore, E_{ad} and E_d can be estimated from the comparison of the experiments to the simulation. Further studies by the simulation changing the parameters are in progress to connect quantitatively simulated results on a molecular scale to experimental results on a macroscopic scale.[11]

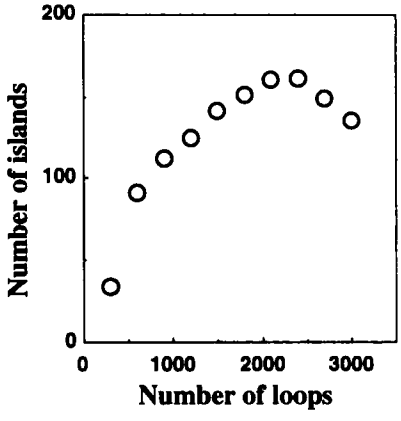

FIGURE 2
Density of islands by simulation

Although islands on them grow larger as the deposition time increases, the shapes and sizes of islands are also different between these three substrates. It can be obtained that the growth rate along each axis of islands by measuring the width (*a*-axis), the length (*b*-axis) and the height (normal to the *ab*-plane) of them as the function of the deposition time. Figure 3(a), (b) and (c) show the changes of the length, width and height of islands of average sizes for the deposition time. The lengths of islands saturates as shown in Fig.3(a) at around 200 seconds because islands collide each other at this stage. The slope of these curves corresponds to the growth rate along each crystallographic directions of TTF-TCNQ. At the very initial stage the growth rates of width are around 5 x 10^{-1}nm/s, 5 x 10^{-1}nm/s and 3 nm/s for the NaCl, KBr and KCl substrates, respectively. The growth rates of length are around 5 nm/s, 9 nm/s and 20 nm/s. The growth rates of height are around 7 x 10^{-2}nm/s, 1 x 10^{-1}nm/s and 3 x 10^{-2}nm/s.

At the initial stage the growth rates of the length and the width for the NaCl substrates are 70 times and 7 times larger than that of height, respectively. For the KBr substrates, they are 90 times and 5 times larger. For the KCl substrates, they are 700 times and 100 times larger. TTF-TCNQ islands grows in much more two-dimensional fashion on the KCl substrates than those on the other two. On the contrary the growth

rates of height for the KCl substrates are smaller than those for the NaCl and KBr. These differences may be explained considering the differences of the surface energy and interfacial energy. In thermodynamics, for three-dimensional (3D) and two-dimensional (2D) growth modes the following relation exists among their energies;[13]

$$\sigma(F) > \sigma(S) - \sigma(FS) \quad \text{for 3D growth}$$
$$\sigma(F) < \sigma(S) - \sigma(FS) \quad \text{for 2D growth}$$

where $\sigma(F)$ is the surface energy of a film, $\sigma(S)$ is the surface energy of a substrate, and $\sigma(FS)$ is the interfacial energy between them. Namely, when $\Delta = \sigma(F) - \sigma(S) - \sigma(FS)$ is smaller, a film grows in more two-dimensional fashion. In this case, when $(\sigma(S) - \sigma(FS))$ is larger , a film grows in more two-dimensional fashion because $\sigma(F)$ is common for these three substrates. Our AFM images revealed that the islands tend to grow on KCl in much more two-dimensional fashion compared with other two substrates. So the following relation can be obtained; $\sigma(S:NaCl) - \sigma(FS:NaCl) < \sigma(S:KCl) - \sigma(FS:KCl)$. The surface energies of these three alkali halides were estimated as 0.438 Jm^{-2} for NaCl, 0.229 Jm^{-2} for KBr and 0.264 Jm^{-2} for KCl, respectively.[14] So $\sigma(FS:KCl)$ is expected to be much smaller than $\sigma(FS:NaCl)$. Since the surface energy of a TTF-TCNQ film, $\sigma(F)$, is not known, it can not be concluded which is large and small between $\sigma(FS:KBr)$ and $\sigma(FS:KCl)$ or between $\sigma(FS:KBr)$ and $\sigma(FS:NaCl)$.

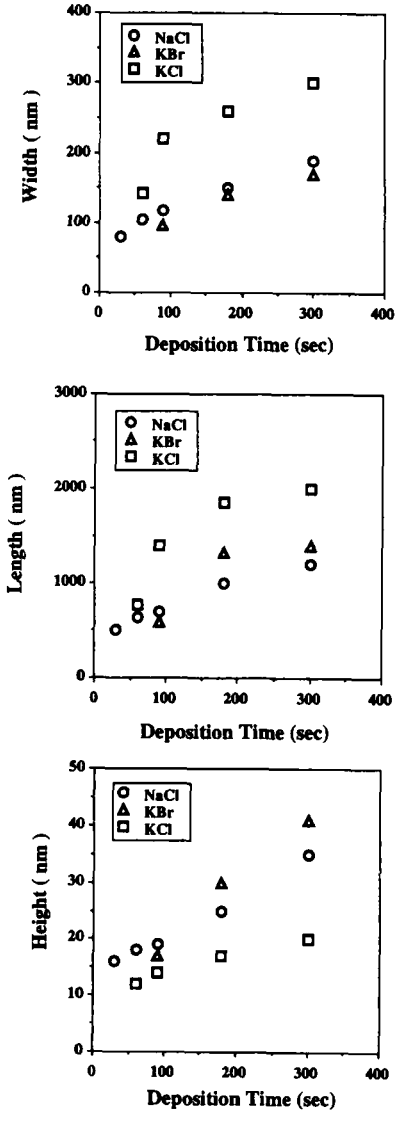

FIGURE 3
Changes of width, length and height of islands by increaseing deposition time

CONCLUSION

The conclusion can be summarized as follows: AFM was applied to study quantitatively anisotropic crystal growth of TTF-TCNQ on three kinds of alkali halides, NaCl, KBr and KCl. It was found that their growth rates along *a*-, *b*- and ***a*** **x** ***b*** are different between all the substrates. This study has revealed that AFM is very powerful to study the crystal growth of organic materials and computer simulation is promising to clarify the mechanism of crystal growth of organic materials on a microscopic scale.

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