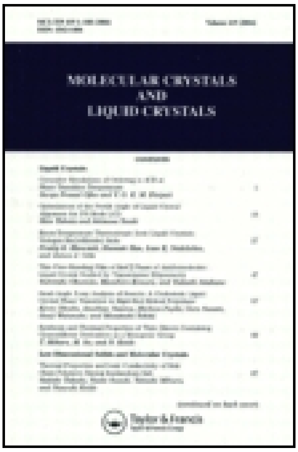

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Strained Lattice Organic Thin Film Growth by Molecular Beam Epitaxy

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STRAINED LATTICE ORGANIC THIN FILM GROWTH BY MOLECULAR BEAM EPITAXY

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Abstract Strained lattice organic thin film which possessed distinct lattice structure from the bulk crystal was formed by molecular beam epitaxy (MBE). *In situ* infrared (IR) spectroscopic characterization was carried out to clarify the as-grown film structure under several growth conditions. The growth condition for parallel orientation of the flat molecules was discussed under the interrelation between the molecule-substrate interactions and the intermolecular interactions.

INTRODUCTION

It is well known that the intermolecular interactions in the molecular crystals are so weak that the crystal lattices alter easily and bear the crystal polymorphism. On the thin film growth of the molecular crystal of π-electron compounds, it was mostly found that the molecules oriented parallel to the substrate surface, ruled by the molecule-substrate interaction. The features of the molecular crystals mentioned above tell us that such oriented molecules on the surface could cause the modifications both on the lateral arrangement and on the stacking structure of the crystal lattice in the film. In this study, *in situ* characterization on the organic thin film growth was carried out under several growth conditions by use of the infrared spectroscopy (IR) to clarify the mechanism of the orientational thin film growth.

IN SITU IR CHARACTERIZATION OF FILM GROWTH

It has been demonstrated that there was a marked difference in the morphology of TCNQ (tetracyanoquinodimethane) films between those grown on HOPG (highly oriented pyrolytic graphite) and those on the surface oxidized Si substrate (SiO_2). Extended plate-like films were observed on HOPG and island polygons on SiO_2 by SEM (Scanning Electron Microscopy) observation.[1] To clarify the origin of the morphological difference of these films, *in situ* characterization of the film growth was carried out by IR reflection absorption spectroscopy (RAS).[2] As a result, an additional differenece was found for the films on HOPG, that is the spectral peak shifts on the out-of-plane intramolecular vibrations.

Figure 1 shows the *in situ* IR spectra for TCNQ films on HOPG grown at various substrate temperatures. Predominance of b_{3u} (the out-of-plane mode) peaks[3] in the RAS spectra indicated the parallel orientation of the flat molecules on the substrate. Furthermore, the b_{3u} peaks showed splittings depending on the growth temperature. Around the room temperature, the peak showed single structure and shifted to lower wavenumber from the position of the bulk crystal. Below the room temperature, another peak appeared at higher wavenumber. The lower the growth temperature, the intenser the high-wavenumber peak became.

On the other hand, *in situ* spectra of the film growth on the SiO_2 substrate did not indicate a preferential manifold orientation of the molecule and the b_{3u} peak showed no splitting over the growth temperature range. This peak position was identical to that of the high-wavenumber peak of the split b_{3u} peak observed on HOPG and to that of the bulk crystal. Therefore, the low-wavenumber b_{3u} peak observred on HOPG indicated the formation of a distinct lattice from the bulk crystal, i.e. a strained lattice, which could be originated from the face-to-face parallel stacks for all of the molecules on the substrate. Such a strained lattice structure could cause variations on the intramolecular vibrations, especially on the vibrational displacements of the out-of-plane modes of the flat molecules. Consequently, anharmonic vibrational potentials of these modes resulted in the spectral peak shifts.

Figure 2 shows the *in situ* spectra observed in the time course of the film growth for chloranil (CA) films on HOPG. In this case, b_{2u} peaks[4] were dominant on the spectra, indicating the standing orientaion of the flat molecule. However, weak b_{3u} (C=O out-of-plane bending) peaks appeared at the very initial stage of the film growth, indicating the parallel orientation of molecules in the initial few layers of the film. This is a marked difference from the case of TCNQ films on the same substrate, HOPG. Weak intensity of the b_{3u} peak of CA molecule could be ascribed to the stiffness of the C=O double bond. The peak positions of the predominant b_{2u} peaks for the thick films were identical to the bulk crystal, suggesting that the molecules might agglomerate to the bulk crystal structure according to the donor–acceptor like intermolecular interactions between the carbonyl groups.

ENERGETIC INTERPRETATION ON THE MOLECULAR ORIENTATION

Experimental results mentioned above suggested that the film structure was ruled by the interrelation between the molecule–substrate interactions and the intermolecular interactions. We have set up a hypothesis that a 2–dimensional lattice film with parallel oriented molecules could be formed when the sum of the adsorption enrgy of the parallel oriented molecule and the lattice energy of the 2–dimensional molecular lattice surpass the lattice energy of the bulk crystal.

Both of these interactions could be expressed as the sum of the dispersion energy, the exchange repulsion energy, and the Coulomb energy. To estimate these energy terms quantitatively, we make use of the molecular simulation program "*POLYGRAF*" (Molecular Simulations Inc.), which incorporates the above three interaction terms as the non–bonded interactions. To calculate the electrostatic interactions, the atomic charges distributed in the molecules and the substrate were estimated by an charge calculation program[5] incorporated in the program. The 2–dimensional lattice energy was calculated by assuming a suspended unit cell with one molecule (neglecting the effect of the substrate). Table 1 shows the calculated results of the energy terms for several combinations beteen molecules and substrates. These results indicated that TCNQ molecule should form a film with parallel orientation on HOPG, but should agglomerate in the bulk crystalline structure on the SiO_2. Additionally, CA should form a film with parallel orientation on HOPG at least for the first layer. There was a good agreement with the experimental results. For multilayer films, it could be assumed that the inherent molecule configuration in the bulk crystal make an important role to determine the molecular stacking structure.

TABLE I Comparison of the energy terms related to the determination of the molecular orientation. (units in kcal/mol)

	Adsorption Energy[A]		2–D Lattice Energy[B]	Paralel Orientation Film Energy[A+B]		Bulk Crystal Lattice Energy	
	HOPG	SiO_2		HOPG	SiO_2	Calc.	Exp.
TCNQ	29.6	17.2	6.3	35.9	23.5	26.4	25.1
CA	29.1	20.3	3.6	32.7	23.9	22.2	23.7

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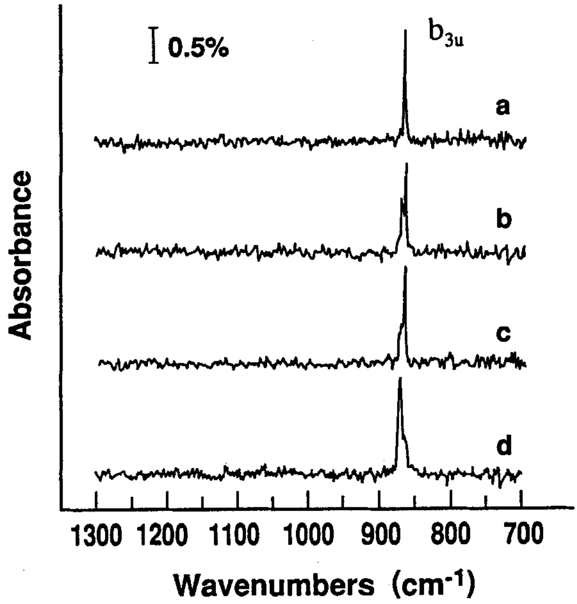

FIGURE 1 *In situ* IR spectra of TCNQ films on HOPG grown at several substrate temperature. The growth temeratures are (a)293K, (b)248K, (c)223K, and (d)154K.

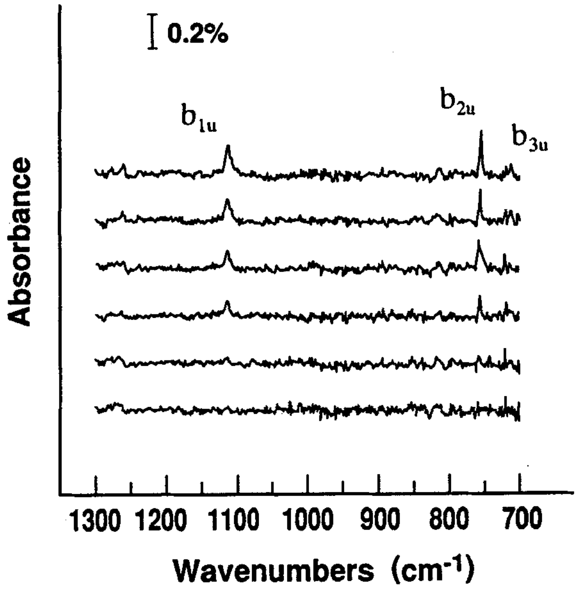

FIGURE 2 *In situ* IR spectra observed in the time course of CA film growth on HOPG.