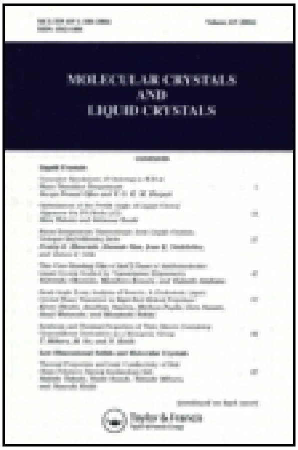

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Epitaxial Relationships of Para-Sexiphenyl Thin Films on Alkali Halide Substrates

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EPITAXIAL RELATIONSHIPS OF PARA-SEXIPHENYL THIN FILMS ON ALKALI HALIDE SUBSTRATES

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The dependence of substrates on the epitaxial relationships of vapor deposited thin films of p-sexiphenyl (p-6P) was investigated by X-ray diffractmetry. The cleaved (001) surfaces of single crystals of NaCl, KCl and KBr were used for the substrate. The temperature dependence of the film structure was also examined between 50°C and 170°C. The epitaxial relationships of both standing and lying orientations were determined for the films grown on each substrate. The observed complex patterns of in-plane orientations were explained in terms of misfit ratio.

Keywords: epitaxial relationships; in-plane orientation; para-sexiphenyl; X-ray diffraction

INTRODUCTION

Para-sexiphenyl (p-6P) is one of semiconducting oligomers having a conjugated system of π-electrons, and is currently attracting great attention as a useful material for opto-electronic devices such as light-emitting diodes and non-linear optical devices [1–5]. To optimize such device performances, the orientation control of the molecules in the thin film state is important,

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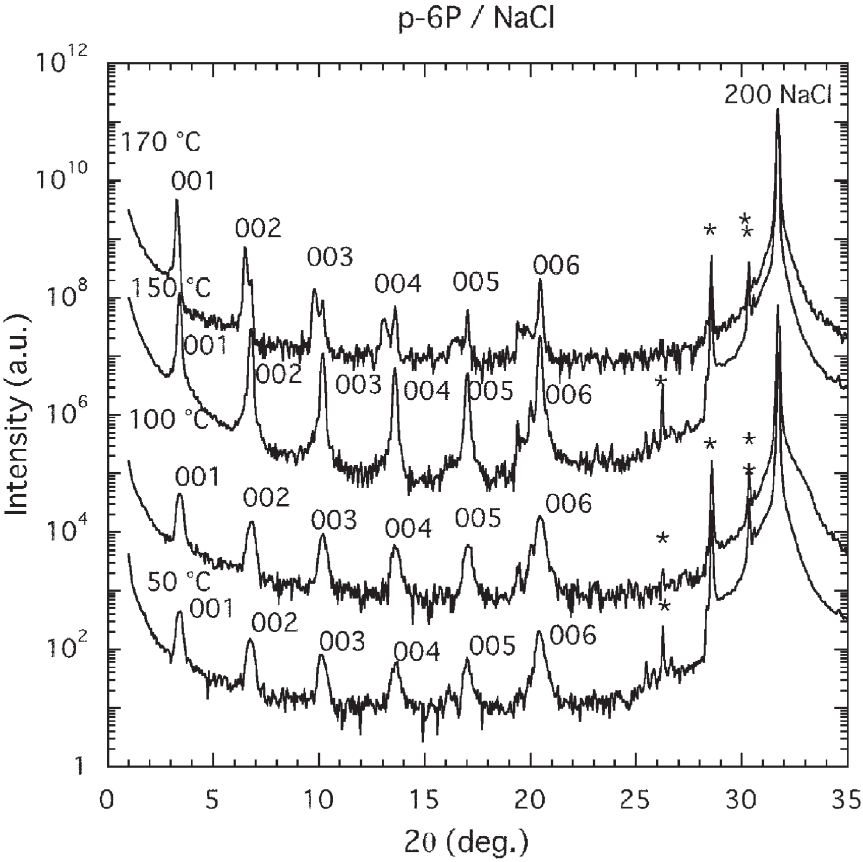

FIGURE 1 Temperature dependence of $\theta/2\theta$ XRD patterns of deposited thin films of p-6P on NaCl substrate.

because their optical properties show significant anisotropy. This is due to the π-electron transition moment is aligned parallel to molecular long axis. To control the molecular orientation, the roles of substrates and growth conditions in physical vapor deposition have been investigated by some research groups [6–9]. From these studies, it was revealed that five kind of orientation patterns, (001), (11-1), (111), (201) and (20-3) orientations, were appeared depending on temperature and substrates. Furthermore, Smilgies *et al*. clarified the epitaxial relationships of (001) and (11-1) orientations for KCl substrate by means of grazing incidence X-ray diffraction using synchrotron radiation [9]. In this study, the dependence of substrates on the epitaxial relationships of vapor deposited thin films of p-6P

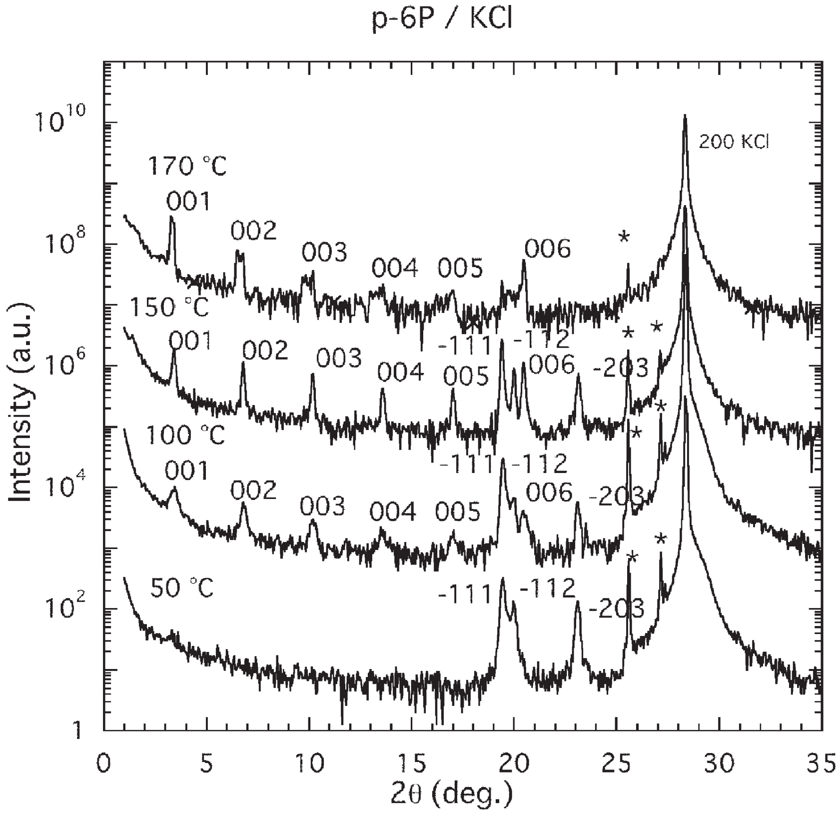

FIGURE 2 Temperature dependence of $\theta/2\theta$ XRD patterns of deposited thin films of p-6P on KCl substrate. The same patterns were obtained for KBr substrate as well.

was investigated for three kinds of alkali halide substrates by X-ray diffractmetry.

EXPERIMENTAL

As the sample, *para*-sexiphenyl (p-6P, Tokyo Chemical Industry Co., 98%) was used without any further purification. p-6P powder was sublimated in a pressure of 5×10^{-5} Pa from K-cell type crucible kept at 200°C. The substrates used were air-cleaved (001) planes of NaCl, KCl and KBr maintained at a temperature between 50 and 170°C after baked at 200°C for

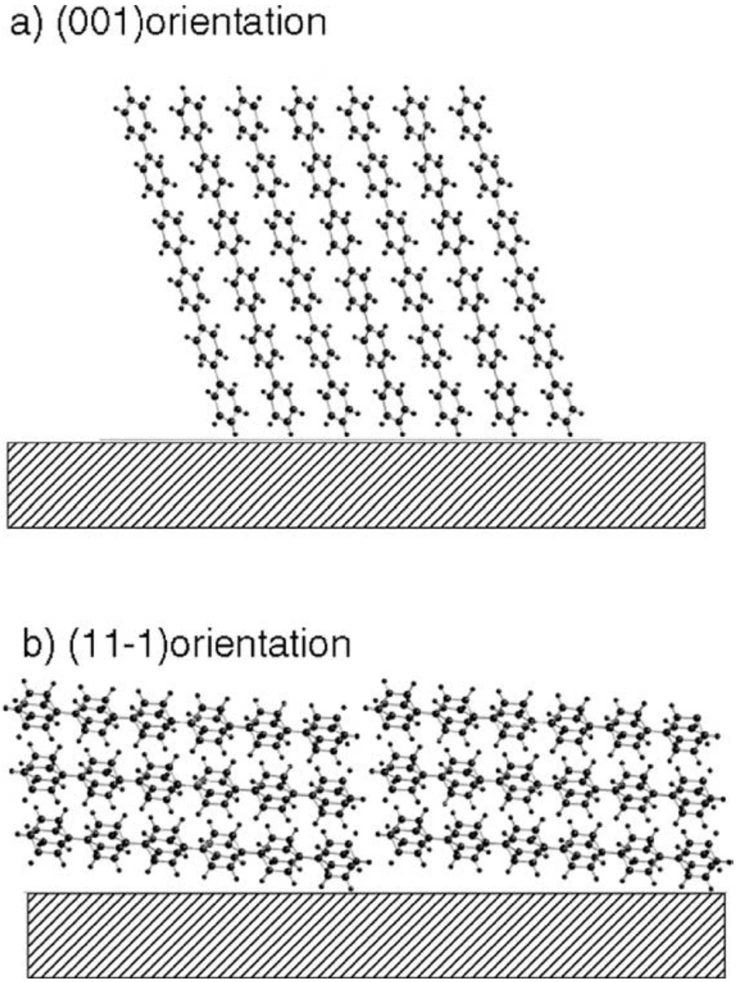

FIGURE 3 Schematic illustration of cross sections of standing (001) and lying (11-1) orientations.

1 hour. The deposition rate and final film thickness were 0.1 nm/s and 100 nm, respectively. The as-deposited thin films were characterized using X-ray diffraction in air using an X-ray diffractometer (Regaku Co., ATX-G) which was specially designed for characterization of thin films. A parabolic multiplayer positioned next to the laboratory X-ray source produces high intensity parallel beam (Cu Kα). The goniometer has not only usual $\omega/2\theta$ axes but also in-plane $\phi/2\theta\chi$ axes for measuring both in-plane and out of

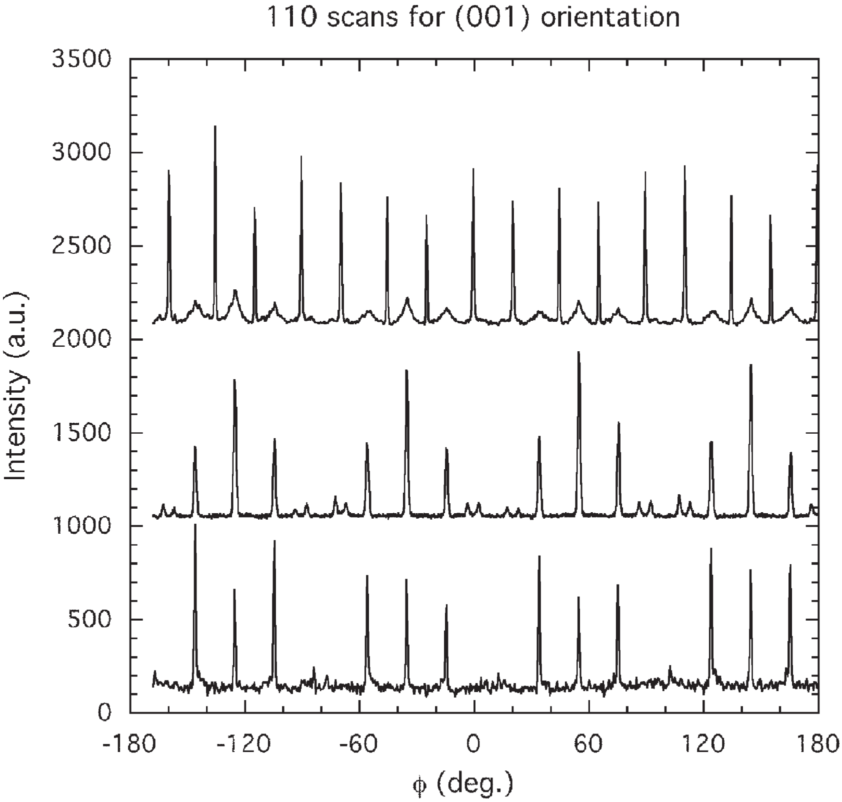

FIGURE 4 In-plane ϕ scan pattern of 110 X-ray diffractions of standing (001) orientation ingredients of p-6P thin films.

plane diffraction. The details of the diffractometer and characterization method were described elsewhere [10].

RESULTS AND DISCUSSION

Figures 1 and 2 shows the conventional $\theta/2\theta$ scan pattern of deposited p-6P films on NaCl (001) and KCl (001) substrates, respectively. As to the KBr substrate, almost the same diffraction patterns were obtained as that of the KCl substrate.The lattice parameters of a bulk single crystal of p-6P is monoclinic, space group is $P2_1/a$, $a = 0.8091\,nm$, $b = 0.5568\,nm$, nm, $c = 2.6241\,nm$ and $\beta = 98.17^\circ$ [1]. On comparison of the observed

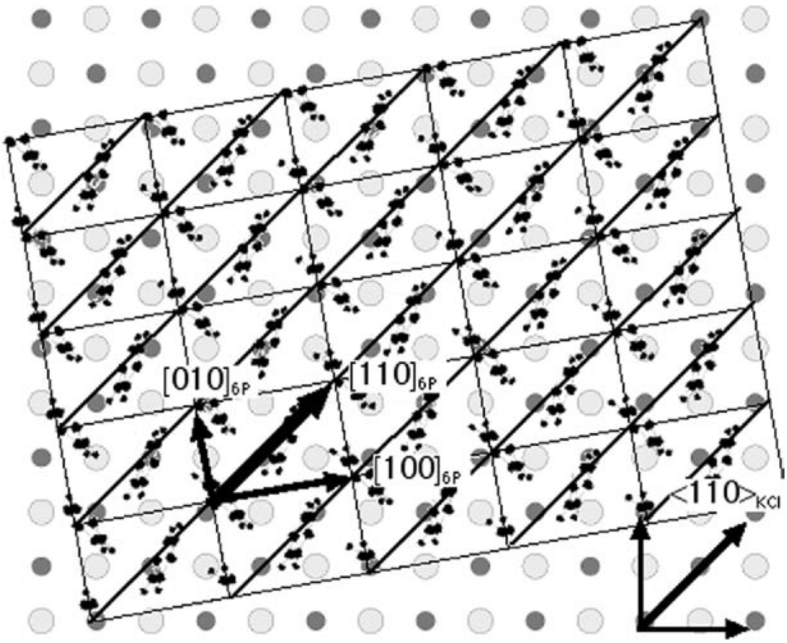

FIGURE 5 Schematic representation of epitaxial relationship between p-6P (001) orientation and KCl.

lattice spacings and the calculated ones, the diffraction peaks in Figures 1 and 2 could be indexed as shown in the figures. The standing (001) orientations and lying orientation (11-1) were appeared depending on temperatures and substrates. The standing (001) preferred at higher temperatures on KCl, KBr substrates. With decreasing temperature, the lying orientation, (11-1) planes parallel to the surface, increased. However, the lying orientation was not found on NaCl substrate even at a lowest temperature (50°C) condition. Figure 3 shows the cross section of the (001) and (11-1) orientations.

As to the in-plane structure, the substrate dependence in epitaxial relationships was found. Figure 4 shows a 110 diffraction pattern from the standing orientation ingredients of a p-6P films formed at 150°C as a function of rotation angle ϕ of substrate normal. From these patterns, the epitaxial relationships were determined as shown in Figures 5 and 6. The determined relationship was $[110]_{\text{p-6P}}//\langle 110\rangle_{\text{KCl}}$ on KCl and KBr substrates. On the other hand, two kinds of relationships, $[010]_{\text{p-6P}}//\langle 110\rangle_{\text{NaCl;}}$ and $[100]_{\text{p-6P}}//\langle 100\rangle_{\text{NaCl}}$, were found on NaCl substrate. As shown in these figure, there exist one-dimensional lattice coordination

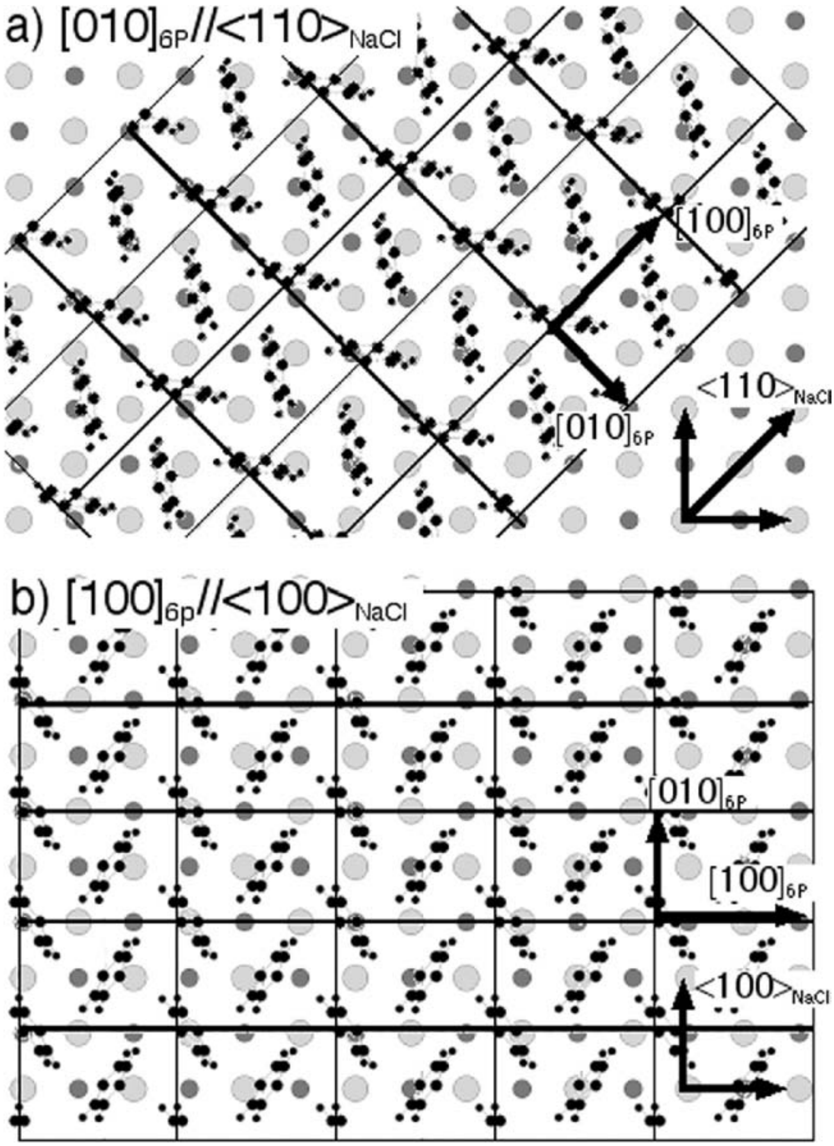

FIGURE 6 Schematic representation of epitaxial relationship between p-6P (001) orientation and NaCl.

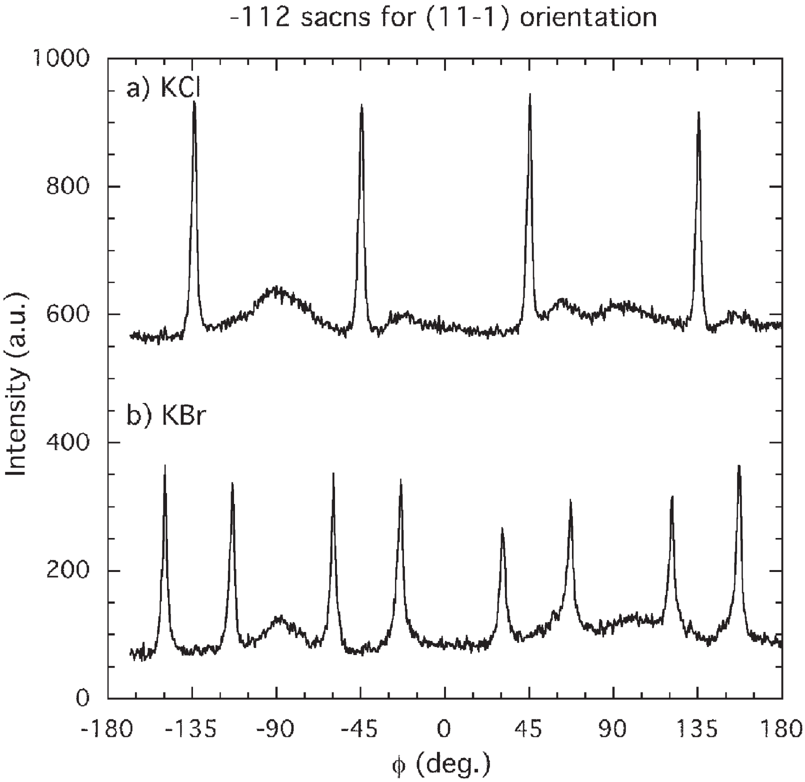

FIGURE 7 In-plane ϕ scan pattern of −112 X-ray diffractions of lying (11-1) orientation ingredients of p-6P thin films.

in [110], [010] or [100] directions, and the misfit ratios between periodicities of p-6P and substrate lattices are 3.6 and 1.3, 1.4 and -0.8%, respectively.

The substrate dependent in-plane orientation was also found in the lying orientation ingredients. Figure 7 shows the -112 diffraction pattern from the lying (11-1) orientation ingredients. As shown in this figure, in-plane orientations of the (11-1) orientation ingredients changed depending on the kind of substrates. The corresponding epitaxial relationships were shown in Figure 8. The determined relationship was $[011]_{p\text{-}6P}//\langle 110\rangle_{KCl}$ and $[101]_{p\text{-}6P}//\langle 110\rangle_{KBr}$, respectively. The one-dimensional lattice coordination was also observed in the lying orientation.

The determined epitaxial relationships were summarized in terms of misfit ratio in (Table 1). In this table, the misfit ratios which appeared actually in the in-plane orientations are calculated and listed with that of

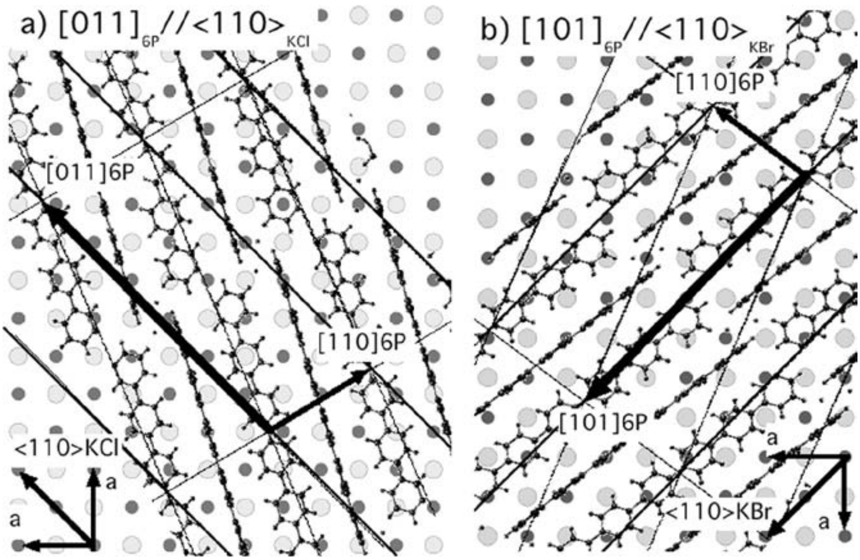

FIGURE 8 Schematic representation of epitaxial relationship between p-6P (11-1) orientation and KCl and KBr.

TABLE 1 Misfit Ratio of Epitaxial Relationships of p-6P (The Misfit Ratios of Appeared Orientation are Underlined)

		Misfit ratio substrate (%)		
Orientation of plane normal	In-plane orientation	NaCl	KCl	KBr
standing (001)	$[110]_{\text{p-6P}}//\langle 110\rangle_{\text{sub.}}$	15.6	*3.6*	1.3
	$[010]_{\text{p-6P}}//\langle 110\rangle_{\text{sub.}}$	*1.4*	−9.1	−13.4
	$[100]_{\text{p-6P}}//\langle 100\rangle_{\text{sub.}}$	*−0.8*	−11.1	−15.3
lying (11-1)	$[101]_{\text{p-6P}}//\langle 110\rangle_{\text{sub.}}$	20.1	7.6	*2.6*
	$[011]_{\text{p-6P}}//\langle 110\rangle_{\text{sub.}}$	13.0	*1.3*	−3.3

possible combinations which were not observed. From this results, it was concluded that the small amount of misfit ratio determine the direction of in-plane orientation of p-6P on alkali halide substrates. The large amount of misfit ratio for the lying orientations on NaCl can be a cause of the absence of lying orientations on it, through the increasing of interfacial energy during the nucleation process.

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