Available online at www.sciencedirect.com
ScienceDirect
Journal of Crystal Growth 310 (2008) 1729–1733
JOURNAL OF CRYSTAL GROWTH
www.elsevier.com/locate/jcrysgro

Orientation of *para*-phenylene crystals nucleated on alkali-halide stepped substrates

H. Yamamoto, H. Takahashi, N. Yano, Y. Takagishi, T. Kubo, T. Harami, H. Hondoh, T. Nakada*

Department of Physical Sciences, Faculty of Science and Engineering, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, Shiga 525-8577, Japan

Abstract

The influences of substrate steps on crystallographic orientation of *para*-quaterphenylene (*p*-4P) thin films deposited on potassium chloride (KCl) (0 0 1) cleaved in ultrahigh vacuum have been studied in needle-shaped crystals preferentially nucleated at the step edges of the substrates. Surprisingly, most of the crystals nucleated on the so-called tartan zone of the KCl (0 0 1) substrate did not grow epitaxially, but became aligned in the directions of the cleaved steps, indicating the onset of grapho-epitaxy. The effects of step height and width on the nucleation and growth of *p*-4P crystals have been discussed.

PACS: 68.35.–p; 68.35.Bs; 68.37.−d; 68.37.Lp; 68.37.Pg; 68.55.–a; 68.55.Ac; 68.55.Jk; 81.15.–z; 81.15.Ef

Keywords: A1. Atomic force microscopy; A1. Crystal structure; A1. Diffusion; A1. Interfaces; A1. Nucleation; A1. Surface structures; A3. Graphoepitaxy; A3. Physical vapor deposition processes

1. Introduction

Para-phenylene (*p*-nP) is a linear π-conjugated molecule, which is one of the several promising materials for light-emitting devices due to their high emission efficiency and chemical stability [1–3]. In order to apply the *p*-nP molecules to light-emitting devices, it is necessary to grow single-crystal thin films on desirable substrates, because of their anisotropic emission property [3–5]. As is well known, the orientation of deposited crystalline thin films strongly depends on the atomic arrangement of the substrates (epitaxy). In addition, the orientation is also affected by the microscopic topography of the substrate surfaces (grapho-epitaxy). For example, the oriented growth of low-molecular-weight polyethylene has been reported on the stepped surface of friction-transferred polymer substrates [6–8]. Furthermore, the grapho-epitaxy of the organic thin films was also observed on amorphous substrates (thermally oxidized silicon) with artificial periodic steps [9]. However, to our knowledge, systematic studies of the effects of surface topography of substrates on organic thin films have not been reported so far.

Alkali-halide single crystals have been widely used as the substrates for epitaxial growth. The surfaces of UHV-cleaved alkali halides have many cleavage steps originated from the interaction between the propagation of the crack front and dislocations [10–15]. Basset and Osaka et al. [15] found that the substrate surface is classified into six areas according to the step direction, height, and density. By using the stepped substrates, systematic discussion about the effects of the steps on the grapho-epitaxy will be made possible. In fact, Osaka et al. [15] revealed the onset of grapho-epitaxy of Sn crystals deposited on NaCl (1 0 0) cleaved in UHV. In this paper, we present the first observation of the grapho-epitaxial growth of *para*-quaterphenylene (*p*-4P) thin films deposited on UHV-cleaved potassium chloride (KCl) (1 0 0). We also discuss the influences of the step height and width on the nucleation and growth of *p*-4P thin films in detail.

---

*Corresponding author.
E-mail address: nakada@se.ritsumei.ac.jp (T. Nakada).

0022-0248/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jcrysgro.2007.11.129

2. Experimental procedure

KCl single crystals for substrates were grown from the melt phase by the Kyropoulos method [16]. KCl powder (99.5%) purchased from Nacalai Tesque was used without any further purification. The surface structure of the UHV-cleaved KCl crystals was observed to be divided into six areas, as reported in previous studies: (1) starting zone, (2) V zone, (3) transition zone, (4) tartan zone, (5) stop-band zone, and (6) restarting zone [10–15]. The starting zone occurs at the initial stage of cleavage and has narrowly spaced small height steps. In the V zone, the number of steps becomes lower, and the area between them is larger. In the transition zone, the steps are aligned parallel to the [1 0 0] direction of alkali-halide substrates. The step height and width increase from the V zone to the transition zone. The tartan zone shows longitudinal steps and flat areas surrounded by these step lines, which run parallel to the [1 0 0] directions. The stop-band zone consists of a high density of transverse lines followed by straight longitudinal lines. The restarting zone follows the stop-band zone and has some features in common with the starting zone [15]. It should be noted that air-cleaved KCl substrates cannot maintain the topography owing to deliquescence [17].

p-4P (98%, Aldrich Chemical) was evaporated on the UHV-cleaved KCl substrates. The deposition rate (about 0.3 nm/min) and thickness (3 nm) were monitored with a quartz crystal microbalance. The base pressure in the evaporation chamber was $\leqslant 10^{-9}$ Torr and the pressure during evaporation was $\leqslant 10^{-7}$ Torr. The substrate surface was kept at room temperature during the evaporation. The surface morphologies of the thin films were observed by atomic force microscopy (AFM; Nanoscope E, Digital Instruments Inc.). The crystal structure and molecular orientation of the *p*-4P thin films were determined by using transmission electron microscopy (TEM; H-7000, Hitachi) and fluorescent microscopy (ECLIPSE E600, Nikon) under maximum fluorescence excitation at $\lambda_{\mathrm{ex}} = 367$ nm.

3. Results and discussion

Fig. 1 shows AFM images of *p*-4P thin films at the initial stages of growth on the starting zone (a), V zone (b), and tartan zone (c). In all of the AFM images, needle-shaped and plate-shaped crystals were observed. Irrespective of the substrate areas, the needle-shaped crystals preferentially nucleated at the step edges. The needle-shaped crystals were rarely nucleated on the starting zone. The needle-shaped crystals appeared to align along the $[1\,1\,0]_{\mathrm{KCl}}$ direction on both the starting zone and V zone. The TEM/TED analysis revealed that the crystals grew epitaxially on the surface, showing the orientation as reported in previous studies on flat KCl substrates [1–3]. On the other hand, needle-shaped crystals tended to align along the $[1\,0\,0]_{\mathrm{KCl}}$ on the tartan zone. The distribution angle of the orientation of the needle-shaped crystals is shown in Fig. 2. These figures clearly show that the needle-shaped crystals arranged along the $[1\,0\,0]_{\mathrm{KCl}}$ directions on the tartan zone, while they grew along the $[1\,1\,0]_{\mathrm{KCl}}$ directions on the V zone. Moreover, the crystals on the tartan zone were not exactly aligned along the crystallographic direction, but were aligned along the direction of the surface steps of the KCl substrates. These characteristics of the needle-shaped crystals grown on the tartan zone suggest that the *p*-4P needle-shaped crystals could grow grapho-epitaxially on stepped KCl substrates.

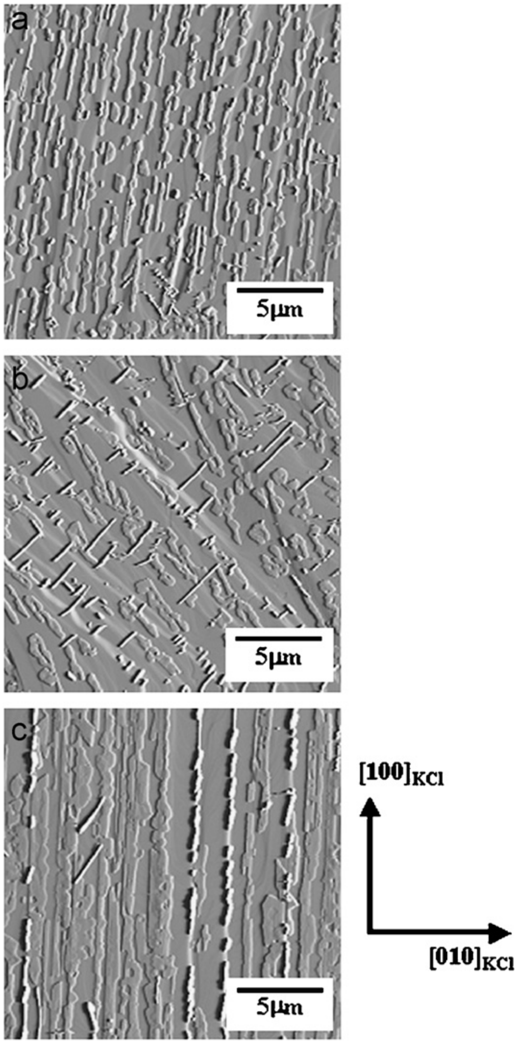

Fig. 1. AFM images of *p*-4P thin films deposited on the starting zone (a), V zone (b), and tartan zone (c) of UHV-cleaved KCl substrates. Needle-shaped and plate-shaped crystals were observed.

Fig. 3(a) and (b) shows an AFM image and corresponding fluorescence image, respectively, of the *p*-4P thin films grown on the tartan zone. Since the electronic transition dipole corresponding to the blue light emission is parallel to the molecular axis, the emitted light radiates in the direction normal to the molecular axis [4,18]. Taking into account the crystal structure of *p*-4P, the *c*-axis of the needle-shaped crystals should be parallel to the substrate surface (lying orientation). A TEM image and selected area electron diffraction pattern (SAED) of *p*-4P thin films