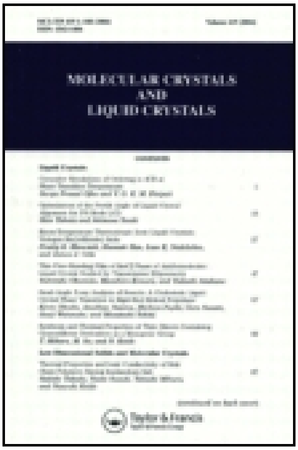

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Dependence of Optical Absorption Spectra on Structures of Bis(1,2-Benzoquinonedioximato)Pt(II) Thin Films

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Structures of the thin film of bis(1,2-benzoquinonedioximato)Pt(II) formed on four kinds of alkali halides by epitaxial growth were analyzed by electron microscopy. The fabricated thin films exhibit new polymorphic structures, the β- and γ-forms. These structures appear depending on substrates used in epitaxial growth and are correlated to the optical spectra of these films.

Keywords: bis(1,2-benzoquinonedioximato)Pt; polymorph; UV-Vis spectrum

INTRODUCTION

One-dimensional d^8-metal complexes with various kinds of 1,2-dionedioxime show interesting electronic and optical properties. The electronic states of the molecular aggregates depend not only on the molecule itself but only on arrangement of molecules. Bis(1,2-benzoquinonedioximato)Pt(II) (Pt(bqd)$_2$, Fig. 1) is known to have an orthorhombic unit cell (α-form;a=2.06nm, b=0.974nm, c=0.635nm) with the shortest Pt-Pt distance of 0.318 nm [1] in the bis(1,2-dionedioximato)Pt(II) family, which leads the absorption of the d-p transition

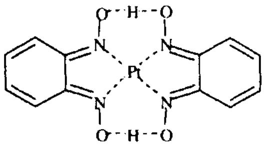

FIGURE1 Chemical Structure of Pt(bqd)$_2$

to the longest wavelength of 1250nm. For thin films of $Pt(bqd)_2$, however, Shirotani *et al.* have reported that absorption spectra of the thin films vary depending on the substrates used for vacuum-deposition [2]. They have suggested an existence of polymorphic structure on NaCl based on their X-ray powder patterns, though the crystal structures of films has not been made clear.

In this report, we discuss the d-p optical absorption bands of thin $Pt(bqd)_2$ films formed by vacuum-deposition on some alkali-halide single crystals from the view point of their structures analyzed in the present work.

EXPERIMENTAL

In order to analyze the structures, epitaxial films of $Pt(bqd)_2$ were made on an (001) freshly cleaved surface of alkali-halide single crystalline substrate (KBr, KCl, KI or NaCl) by vacuum-deposition. The substrate temperature was kept at 25°C. The thickness of films was controlled to be about 30nm.The crystal structures of fabricated thin films were examined by direct molecular imaging using a high resolution transmission electron microscope (HRTEM), electron diffraction and θ-2θ X-ray diffraction methods.

RESULTS AND DISCUSSION

The fabricated thin films epitaxially grown on the alkali-halide substrates exhibit some polymorphic structures. Fig. 2 shows a selected area diffraction (SAED) and the corresponding HRTEM image of the deposited film on KI substrate. The diffraction pattern in Fig. 2(a) can not be interpreted with the already analyzed orthorhombic α-form. The pattern exhibits clearly the existence of a new polymorph having tetragonal structure named here as γ-form on KI. The HRTEM shown in Fig. 2(b) also shows such tetragonal structure. The unit cell dimensions

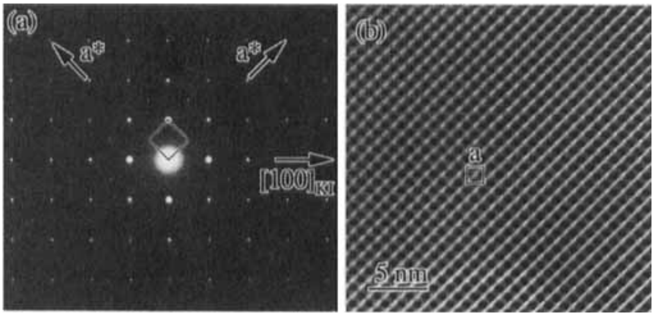

FIGURE2 An electron diffraction pattern (a) and a high resolution image (b) of Pt(bqd)$_2$ (γ-form) deposited on KI. The beam direction was perpendicular to the film surface.

of the γ-form were determined to be a=1.42nm, c=0.656nm based on the electron and X-ray diffraction patterns. The a-axis of the γ-form orients along the [110]-direction of KI. The expected molecular packing of the γ-form is shown in Fig. 3. As the case of the α-form, the molecules form one-dimensional stacking column in the γ-form keeping their molecular planes perpendicular to the column axis coincident with c-axis. The c-axis stands perpendicular to the KI surface and the molecular planes are almost paralleled to the substrate surface. Therefore, the d-p transition is not observed in optical absorption spectrum when the incident light transmits perpendicular to the film surface.

In contrast to the above facts, the deposited films on NaCl, KCl and KBr show another polymorph (β-form). From SAED pattern as shown in Fig. 4(a), two-dimensional rectangular unit cell dimensions of a=2.57nm and c=0.369nm can be determined for the polymorph named as the β-form

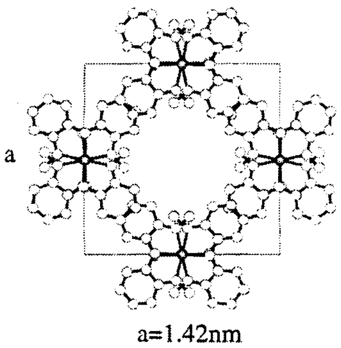

FIGURE3 Expected crystal structure of γ-form of Pt(bqd)$_2$ projected along the c-axis.

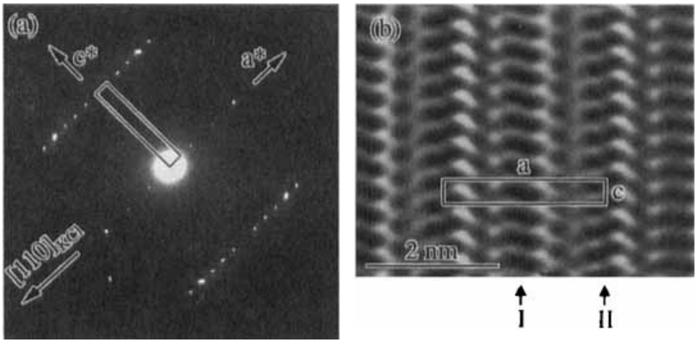

FIGURE 4 An electron diffraction pattern (a) and a high resolution image (b) of $Pt(bqd)_2$ deposited on KCl.

The third dimension of the unit cell, *b*=0.66nm was obtained by X-ray diffraction. The *b*-axis is perpendicular to the substrate surface. Though the detailed structure analysis will be reported elsewhere, HRTEM image of the new β-polymorph (Fig. 4(b)) clearly show that the molecules stack in columns (I, and II in Fig. 4(b)) in which the molecular planes are nearly perpendicular to the substrate surface, because the molecular images in the columns I and II are observed as rod-like contrasts. In the column, the molecular planes have an inclination angle of about 70° with respect to the column axis as shown in Fig. 5. The Pt-Pt distance in this β-form was 0.369nm along the column direction (*c*-axis), so that the strong Pt-Pt interaction as in the α-form is not expected. The molecular column aligns along the [110]-directions of the substrates. The β-polymorph is thermally unstable,

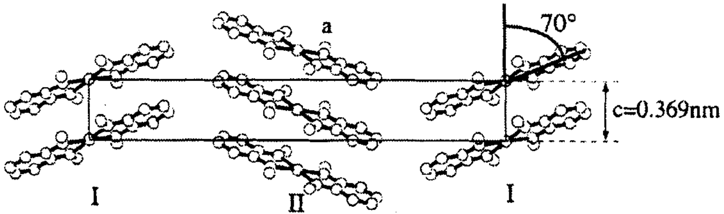

FIGURE 5 Crystal structure model of the β-form on KBr, KCl and NaCl.

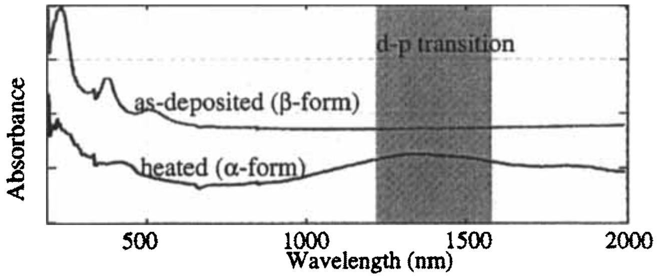

FIGURE 6 Change in absorption spectrum of film on KCl before and after heating. Such spectral change has been already reported by Shirotani *et al.*[2]

because it transforms easily into the ordinary α-form by heating, as shown in absorption spectra of Fig. 6. The β-form does not show the absorption caused by d-p transition owing to the longer Pt-Pt distance, even though the column axis is perpendicular to the incident direction of light. After heating, however, the d-p transition peak appears at 1250nm, since the Pt-Pt distance became shorter in the α-form and the column axis of the α-form was found to align in the same direction to that of the β-form after the transition. On KBr, however, the β-polymorph transforms more easily into the ordinary orthorhombic α-form. It occurs even at room temperature.

Such the easiness of transformation on KBr can be interpreted as follows. The epitaxial orientation angle and its regularity of the β-form crystals relative to the substrates can be understood by the concept of point-on-line coincidence [3]. In the point-on-line epitaxy, some lattice planes of the deposited crystal tend to align in parallel with a basic lattice line of substrate surface. In the present case, the {110}-spacing of the substrate was assumed as such the basic lattice line and lattice misfits were calculated for this spacing and several lattice intervals of β-form $Pt(bqd)_2$ having nearly the same spacings with that of the {110} of alkali halides (Table 1). From the table, we select the cases of negative values of misfit for every substrate, because the positive misfit means that the unit cell of deposited layer should be compressed at the

	{110} spacings of alkali halides	lattice spacing of β-form to coincide with the {110} of substrate	misfits
NaCl a=0.563nm	d_{110}=0.398nm	d_{600}=0.428nm d_{001}=0.369nm	+7.5% -7.3%
KCl a=0.629nm	d_{110}=0.445nm	d_{500}=0.514nm d_{600}=0.428nm	+15.5% -3.8%
KBr a=0.660nm	d_{110}=0.467nm	d_{500}=0.514nm d_{600}=0.428nm	+10.1% -8.4%

TABLE 1 Here the misfits are evaluated by misfit=$(d_{dep}-d_{sub})\times 100$ / d_{sub}, where d_{sub}=the{110} spacing of alkali halides and d_{dep}=the corresponding lattice spacing of $Pt(bqd)_2$

interface in order to achieve the complete point-on-line coincidence at actual interface but it may, in general, be energetically unfavorable. Consequently, the most smallest negative misfit for each substrate realizes as the epitaxial orientation. Indeed, for all substrates the a-axis (or *c*-axis) of the β-form orients along the [110]-direction of the substrate. Moreover, the misfit value can be considered as a measure of distortion of crystal lattice at the interface. Accordingly, the smallest value of -3.8% on KCl indicates the most favorable of orientation while the value of -8.4% on KBr the worse. The large misfit for KBr than for KCl and NaCl may relate to easiness of the transformation of the β-form to the ordinary α-form at room temperature. This difference in distortion was observed as the difference in arcing of reflection spot in electron diffractions (not shown here).

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