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Takeo Suga [a], Seiji Isoda [a], Takashi Kobayashi [a], Masato Isogai [b] & Michael Engel [b]

[a] Institute for Chemical Research, Kyoto University, Uji, Kyoto, 611-0011, Japan

[b] Hitachi Research Laboratory, Hitachi Ltd., 7-1-1, Omika, Hitachi, Ibaraki, 319-1221, Japan

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Structure and UV-VIS Spectra of Nitrido(Phthalocyaninato)Rhenium(V) (ReNPc) Thin Film

TAKEO SUGA[a], SEIJI ISODA[a], TAKASHI KOBAYASHI[a], MASATO ISOGAI[b] and MICHAEL ENGEL[b]

[a]*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611–0011, Japan and* [b]*Hitachi Research Laboratory, Hitachi Ltd., 7–1–1, Omika, Hitachi, Ibaraki 319–1221, Japan*

ReNPc thin films were grown epitaxially on alkali halide single crystalline substrates with different orientations depending on the substrates. Based on electron diffractions, the following two dimensional square lattice units were determined; $a \approx c \approx 2.54$ nm for the γ-form and $a \approx b \approx 1.39$ nm for the β-form as the projection perpendicular to the film surface. Their Q-bands showed prominent absorption bands depending on the film thickness. The result reveals the existence of a new stress-relaxing phase between the two polymorphs, β- and γ-forms appearing at the different thickness.

Keywords: ReNPc; thin film; vapor deposition epitaxy; crystal structure; polymorph; UV-VIS spectra

INTRODUCTION

Recently phthalocyanine complexes have been recognized as functional materials such as non-linear optical and sensing materials. Preparation of such thin films by molecular beam epitaxy (MBE) or vapor deposition epitaxy (VDE) is considered to be important to accomplish electronic and optical anisotropies. In these thin films, UV-VIS absorption spectra of some phthalocyanines are known to change corresponding to their film thickness and also to depend on the substrates used[1-3]. In these reports,

the changes of the electronic state have been expected in accordance with the change of crystal structures.

ReNPc is an interesting molecule because it has a triple bond between the rhenium and the nitrogen ligand. However, there have been a few studies on ReNPc[4–7] and its crystal structure has not been reported.

In this study, we prepared ReNPc thin films by VDE and measured the thickness dependence of UV-VIS spectra, which will be discussed in relation to the change of their structures.

EXPERIMENTAL

ReNPc thin films with various thickness were prepared epitaxially on the cleaved (100) surface of alkali halide single crystals (KCl, KBr) by VDE. During the preparation of thin films, the pressure of a vacuum chamber and the temperature of substrates were kept at 1×10^{-4} Pa and 175–200 °C, respectively.

Structures of the epitaxial films were examined by electron diffraction using a transmission electron microscope (TEM) with an accelerating voltage of 200 kV after the removal of alkali halide substrates. UV-VIS spectra were measured for the films as-deposited on substrates.

RESULTS AND DISCUSSION

Electron diffraction shows that thin ReNPc formed on KCl substrate exhibits two types of crystal structures (Figure 1(a)). Though the diffraction patterns seem intricate, they could be assigned to two structures. One is named as γ-form, which is similar in structure to the C-type of titanyl phthalocyanine (monoclinic, *Cc*, a = 2.519, b = 0.385, c = 2.546 nm, $\beta = 90.3°$)[8]. In the present case, the γ-form has a square lattice of $a \approx c \approx 2.54$ nm, which was found in relatively thicker films. On the other hand, the other crystal form, β-form, appeared predominantly in thinner films. The unit cell of the β-form has almost a half of the γ-form; $a \approx b \approx 1.39$ nm. As for the orientations of each crystal structure, the directions of the a-axes of both crystals are almost parallel to the [012] axis of KCl.

On KBr substrate (Figure 1(b)), the diffraction pattern shows again two crystal forms (γ and β) whose structures are the same with those

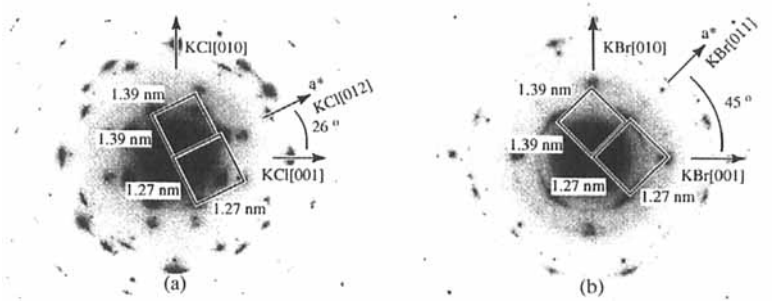

FIGURE 1 The electron diffraction patterns of ReNPc thin films; deposited on (a) KCl and (b) KBr.

on KCl. The epitaxial orientation is different from that on KCl. The directions of the a-axes of both forms on KBr are almost parallel to the [011] axis of KBr. The details of their orientations are not described here, but its difference can be explained by *point-on-line coincidence*[9].

The profiles of UV-VIS absorption spectra of the thin films change with the film thicknesses as shown in Figure 2, where the spectra are normalized so as for the absorption peak at around 340 nm to be unity. It can be seen that UV-VIS spectra definitely change their peak positions and intensities with the film thickness. The Q-bands in 600–800 nm are known to alter their shapes under different circumstances around a molecule, because these Q-bands are assigned to the π-π^* transitions of the phthalocyanine ligand[10]. In the present case, with decreasing thickness the absorption around 630 nm decreases its intensity, but the peak intensity around 760 nm increases monotonously. In addition to these changes in the intensities, an additional absorption peak at 820 nm appears strongly at t = 4.5 nm.

Considering the structure changes from the β-form to the γ-form with increasing thickness, the peak around 630 nm can be assigned to be due to the γ-form structure, and the peak around 760 nm to the β-form. The β-form is, therefore, formed firstly on substrate and later turns into the stable γ-form. However, the change in the shape of the band around 820 nm shows the maximum in relative intensity at t = 4.5 nm, so that an existence of a third phase would be taken into consideration. We do not

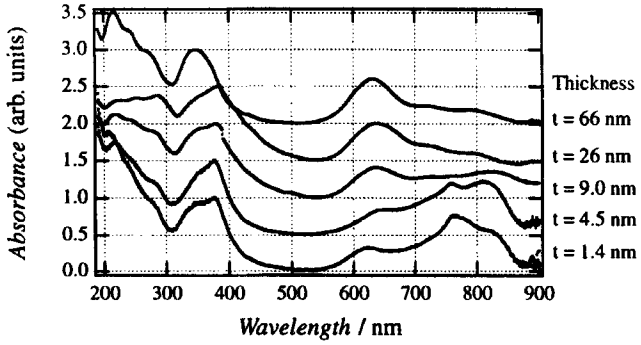

FIGURE 2 UV-VIS spectra of ReNPc thin films with various thicknesses on KCl. Each spectrum is shifted along the vertical axis for clarity.

have any crystallographic evidences on the third phase, but it is plausible to consider that the third phase may be a transient phase between the β- and γ-forms. In the course of crystal growth, the a-axis of β-form, 1.39 nm, becomes shorter to 1.27 nm (a half of a-axis in γ-form), and such change should happen gradually in a transient layer which is considered to be the third phase here. Of course, this phase is not "crystallographic phase", but a stress-relaxing layer. These spectral changes are concluded to be resulted from these different phases realized in thin films of ReNPc.

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