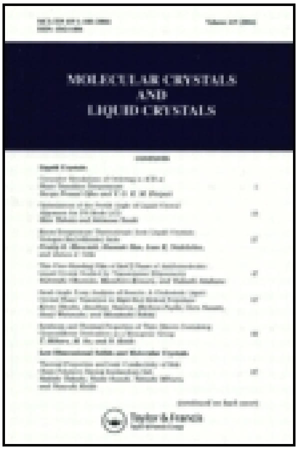

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Structural Aspects of Reversible Control of Optical Activities of Bis(dimethylglyoximato)platinum(I

Thin Film

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Structural Aspects of Reversible Control of Optical Activities of Bis(dimethylglyoximato)platinum(II) Thin Film

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By iodine doping, the structure of Pt(dmg)$_2$ is changed from the orthorhombic with one-dimensional metal chain to an amorphous-like state, which means that the doping induces fluctuation of metal-metal distance along the chain axis. This structural change is reversible; that is, the amorphous state turns back to the orthorhombic crystal by heating at 130°C, corresponding to the reversible change in optical properties.

Keywords: bis(dimethylglyoximato)Pt; iodine doping; reversible change; structure; optical properties; cryo-TEM

INTRODUCTION

Recently Kamata *et al.* have demonstrated reversible controllability of the third-order nonlinear activity of bis(dimethylglyoximato)Pt(II), abbreviated hereafter Pt(dmg)$_2$, by exposing to gaseous iodine and reversely by heating at 130°C [1]. The molecule has the planar chemical structure as shown in Fig.1, which stacks parallel with an adjacent staggering angle of 90° in crystal. In such kind of metal complexes, an absorption band due to the $d_z{}^2$-p_z transition in the linear metal chains is observed in the visible region [2].

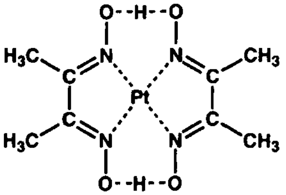

FIGURE 1 Chemical structure of Pt(dmg)$_2$.

In the present paper, we report the structural aspects of the reversible change of the optical properties by electron microscopy and X-ray measurement.

EXPERIMENTAL

In order to examine the structural changes induced by iodine doping, well-oriented epitaxial films of Pt(dmg)$_2$ were fabricated by vacuum-deposition on the (001) cleaved surfaces of alkali-halide single crystals (KCl, KBr and NaCl) and mica. In addition to those, a fused silica glass was used as the reference substrate, since Kamata *et al.* have used the glass plate as the substrate. These substrates were kept at 70°C during the vacuum-deposition. The iodine doping was carried out at 20°C by exposing gaseous iodine for several hours.

Since the doped iodine was found to be very easily released from the film under vacuum, the electron microscopic observation of the doped samples was mainly performed with a low temperature transmission electron microscope (Cryo-TEM, JSFX-4000 having a low temperature stage cooled down to 4.2K).

RESULTS AND DISCUSSION

The structure and orientation of the deposited films were examined by electron microscopy. Selected area electron diffraction (SAED) patterns taken from the deposited films of Pt(dmg)$_2$ on all substrates can be indexed from the orthorhombic structure of **a**=1.6821, **b**=1.0558 and **c**=0.6513nm=stacking chain axis[3]. In the case of KCl (or KBr), the crystal grows with the chain axis perpendicular to the substrate surface. On NaCl substrate, however, the crystal grows mainly making its **c**-axis parallel to the substrate surface. On mica and fused silica glass, the crystals grow with their chain axes parallel to the surface as in the case of NaCl, without any definite in-plane orientation at interface. The result on the epitaxy will be published elsewhere and we will not go further into the details here.

Owing to the different orientation of the metal-metal chain, the optical absorption spectra exhibit different features, when the incident beam transmits perpendicular to the deposited film surface. As shown in Fig.2(a), a strong absorption peak is observed around 690nm for the films deposited on NaCl, mica or glass, which corresponds to the d-p transition. On the other hand, this peak was not observed for the film on KBr or KCl due to the perpendicular

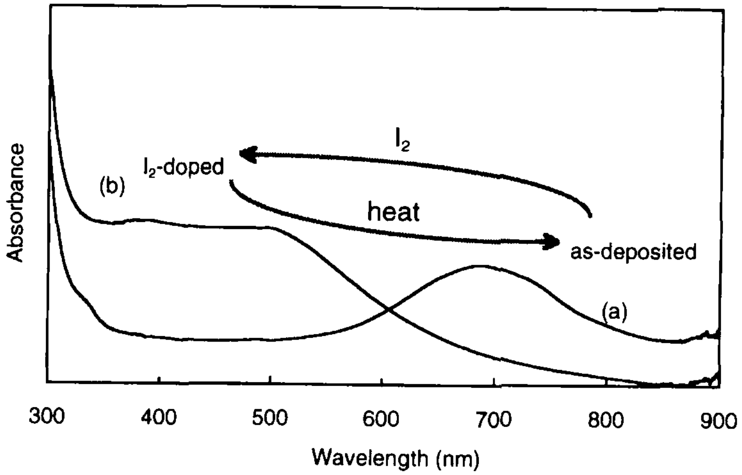

FIGURE 2 Absorption spectra of as-deposited (a) and iodine doped (b) films fabricated on NaCl.

orientation of the transition dipole moment.

By iodine doping, as shown in Fig.2(b), the Pt(dmg)$_2$ film deposited on NaCl, mica or fused silica glass changed its color and also $\chi^{(3)}$ value as reported by Kamata *et al.* [1]. The SAED patterns of iodine doped films were observed at low temperatures around 10K, so as not to release iodine from the sample in the vacuum of electron microscope. As a result, the orthorhombic diffraction spots observed in SAED became diffuse, which means that the structure turns into an

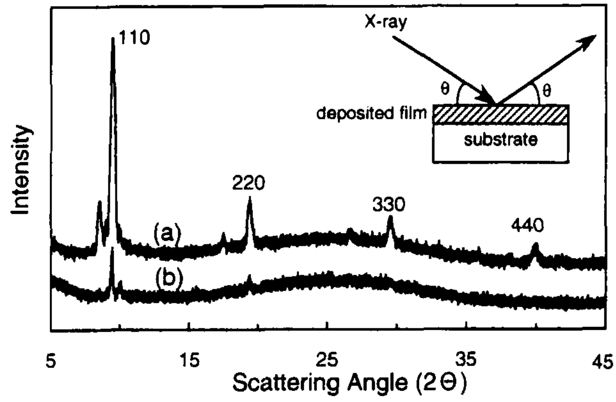

FIGURE 3 X-ray diffraction pattern with CuKα,β taken from Pt(dmg)$_2$ deposited on glass plate (a), and iodine doped (b). In (a), hk0-reflections are only observed due to the epitaxial growth.

amorphous by iodine doping. Such structural change can also be observed in X-ray diffraction as shown in Fig.3; Crystalline diffraction peaks observed initially for the as-deposited samples became weaker and weaker with doping. Correspondingly the absorption peak at 690nm due to the d-p transition in the metal chain disappeared with increasing the amount of iodine doped. Reversely the absorption peak reappeared after heat treatment at 130°C, and the orthorhombic diffraction spots appeared again in SAED and X-ray, even though the epitaxial orientation was a little confused compared with the original one. Accordingly the absorption peak reappeared at 690 nm after desorption. Also in the films formed on KCl and KBr, the structural change between the orthorhombic and the amorphous was reversible as well.

Diffraction experiments clearly showed that the one-dimensional stacking of Pt(dmg)$_2$ molecules turned into a random or distorted one as illustrated in Fig.4. This implies that the iodine invades into the crystal to form a complex, resulting in the disruption in metal-metal chain.

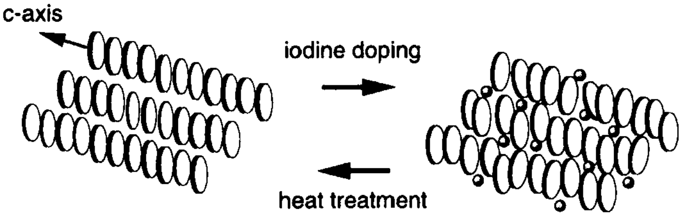

FIGURE 4 A model of the structural change by iodine doping; one-dimensional regular molecular packing (left) and distorted alignment due iodine doping (right).

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