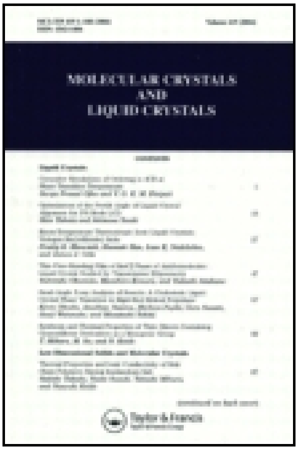

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Effects of Various Deposition Conditions on the Structure of Platinum Complex Films

Takanori Tano [a], Takehito Kodzasa [a], Hirobumi Ushijima [a] & Toshihide Kamata [a]

[a] National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki, 305-8565, Japan

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Effects of Various Deposition Conditions on the Structure of Platinum Complex Films

TAKANORI TANO, TAKEHITO KODZASA, HIROBUMI USHIJIMA and TOSHIHIDE KAMATA

National Institute of Materials and Chemical Research, 1–1 Higashi, Tsukuba, Ibaraki 305–8565, Japan

Effects of various deposition conditions on the structure of thin film of bis-(diphenylglyoximato)platinum(II) on a quartz substrate was investigated by UV-vis spectroscopy and X-ray spectrometry. It was shown for the first time that a control of substrate temperature permits the fabrication of a thin film with perpendicular orientation of the metal chains on a quartz substrate.

Keywords: bis(diphenylglyoximato)platinum(II); structure; polymorph; one-dimensional metal complex; organometallic complex

INTRODUCTION

It has been known that bis(diphenylglyoximato)platinum(II), (Pt(dpg)$_2$, Figure 1), in the evaporated thin film has strong metal-metal interaction forming a columnar structure in a solid state. The columnar structure is effective to show several optical properties, such as third-order nonlinear optical properties. Thus the orientation control of the column is important to improve the optical properties. Previously we have found that the metal chains in an evaporated film of dioxime complexes of d^8 transition metals on a glass substrate usually orient parallel to the surface[1]. Moreover, we have shown that the lattice matching between film molecules and substrate surface were needed to fabricate thin films with perpendicular orientation of the metal

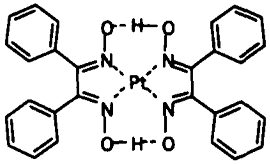

FIGURE 1 Molecular structure of Pt(dpg)$_2$.

chains[2]. In this study, we have examined the possibility if the column orients perpendicular to the film surface on a glass substrate. It was found that perpendicular orientation of the metal chains could be obtained by controlling substrate temperature although it was not in the lattice matching condition between deposited molecules and substrate surface.

EXPERIMENTAL

Thin films of $Pt(dpg)_2$ were prepared by conventional vacuum evaporation onto a fused quartz substrate. The sample chamber was evacuated at ca. 10^{-7} Torr. Substrate temperatures were varied between 30 and −175 °C, and deposition rates were changed from 10 to 0.1 nm/min. The film thickness, measured with a Tencor Alpha-step 300 surface profilometer, was from 100 to 150 nm. Absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer in a wavelength range 300-1000 nm. A p-polarized UV beam through a Glan-Thompson prism was incident upon the film at an angle of 70°. X-ray diffraction (XRD) patterns were obtained by a Mac Science MXP-18 diffractometer with Cu-Kα radiation.

RESULTS AN D DISCUSSION

Figure 2A shows the absorption spectrum of $Pt(dpg)_2$ films prepared at −175 °C with an evaporation rate of 0.19 nm/min. At normal incidence, only one band was observed at 387 nm, assigned to the metal-to-ligand charge transfer transition[3]. We have revealed that $Pt(dpg)_2$ film made with the same deposition rate at room temperature gave a green phase with strong absorption band at 700 nm[4,5]. This band is assigned to the $5d_z{}^2$-$6p_z$ transition of platinum that originates in the d-orbital overlap between adjacent platinum ions in the linear metal chain[3]. The transition moment of 700 nm band is parallel to the metal chain. Therefore, molecular orientation change of $Pt(dpg)_2$ in the film is a possible explanation for absence of this absorption in Figure 2A. To investigate this, polarized absorption spectra with oblique incidence of source beam were measured. Obtained result is shown in Figure 2A (dotted line). A strong broad band could be observed at 700 nm with a shoulder around 550 nm. This shows that the film composed of green phase and that the Pt(dpg)$_2$ molecules are stacked as its axis is almost perpendicular to the substrate surface.

To investigate the molecular arrangement of Pt(dpg)$_2$ in the green film in further detail, we applied XRD measurements. No sharp line was observed. This indicates that the green film prepared at a substrate temperature of −175°C has no periodic structure for the most part. Therefore, we concluded that most parts of the green film composed of micro crystallites in which the molecular columnar axis orients almost perpendicular to the substrate.

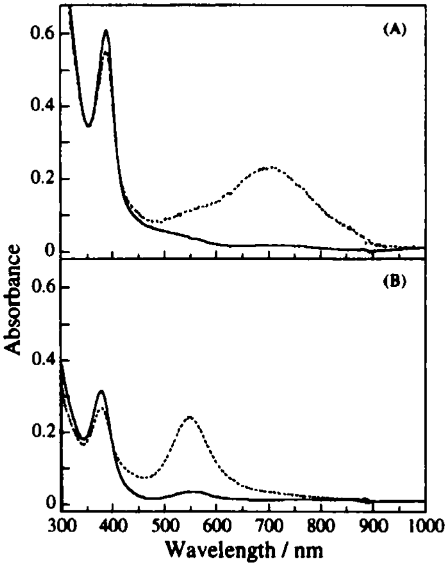

FIGURE 2 Absorption spectra of Pt(dpg)$_2$ film prepared at −175 °C with a evaporation rate (A) 0.19 and (B) 2.1 nm/min. The solid line is the spectrum of normal incidence; the dotted line is that of 70° incidence from the surface normal.

We have found that Pt(dpg)$_2$ has two phases (green and red) in a thin film and the appearance of these phases could be controlled by deposition rate. To study whether this molecular arrangement is a unique characteristic of the green film, we also examined the red film. Figure 2B shows absorption spectrum of Pt(dpg)$_2$ films prepared at −175 °C with an evaporation rate of 2.1 nm/min. At normal incidence, two major bands appeared at 387 and 550 nm in the spectrum. The assignment of 387 nm band is same as that of the green film[3]. The 550 nm band results in the same mechanism as 770 nm band of the green film[3]. When the film was obliqued at 70°, p-polarized absorption spectrum was measured and the result is shown in Figure 2 B (dotted line). A large dichroism was observed. To estimate this quantitatively, the absorption intensity ratio A_p/A_T of the band between p-polarized and normal incident spectra was examined. It has been

TABLE 1 Dichroic ratios at various substrate temperatures.

Temperature / °C	green film (at 700 nm) ≤ 0.50 nm/min	red film (at 550 nm) ≥ 2.0 nm/min
30	1.0	0.90
-60	3.8	6.4
-100	11.6	10.5
-175	12.9	9.7

known that this ratio indicates the degree of band orientation in the film[4]. A_p/A_T of the 550 nm band in the red film was ca. 9.7, and that of the 700 nm band in the green film was ca. 12.9. Therefore, this result reveals that the $Pt(dpg)_2$ molecules in the red film are also stacked as its axis is approximately perpendicular to the substrate surface.

To clarify the temperature range where the film has a unique molecular stacking mentioned above, the absorption intensity ration A_p/A_T of the band was measured. The obtained results are shown in Table 1. It is apparent from Table 1 that as the substrate temperature decreases the dichroic ratio tends to increase and saturates at ca. −100°C in each film. Therefore, it can be said that the metal chain in the film comes to orient perpendicular to the surface at least below −100°C.

Moreover, we tried a thin film of bis(dimethylglyoximato)platinum(II), $Pt(dmg)_2$, where phenyl group of $Pt(dpg)_2$ is substituted for methyl group. Unfortunately, $Pt(dmg)_2$ film did not show the ability like $Pt(dpg)_2$ film. This result strongly suggests that the interaction energy between film molecules and a quartz substrate is one of important factors to cause a unique orientation of molecules in the film mentioned above.

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