Fabrication of a Superstructured One-Dimensional Alloy in a Thin Film Using Bis(dimethylglyoximato)metal(II)

Toshihide Kamata,*,† Takehito Kodzasa,† Hirobumi Ushijima,†
Kaoru Yamamoto,‡ Toshiaki Ohta,‡ and Siegmar Roth§

National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan; School of Science, The University of Tokyo, 7−3−1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan; and Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

Received July 6, 1999. Revised Manuscript Received January 18, 2000

We have investigated the fabrication of a superstructured one-dimensional alloy using bis(dimethylglyoximato)metal(II) ($M(dmg)_2$, M = Pd, Pt) with a vacuum evaporation technique. It was found that coevaporation of these metal complexes gave a thin film of their mixed crystal. The films were quite transparent showing a strong $d_{z^2}-p_z$ transition band in the visible region, of which the peak wavelength subsequently varied in proportion to the mixing ratio. These results suggested that a linear alloy chain was formed in the film of the mixed crystal. A perpendicular orientation of the alloy chain axis could be obtained by depositing the mixed crystal on a KBr-cleaved surface. These findings make it possible to fabricate a one-dimensional superlattice in which several metal components are artificially arranged in a linear chain as designed. $Pt(dmg)_2$ and $Pd(dmg)_2$ were alternatively deposited on a KBr-cleaved surface. Peak shifts of the $d_{z^2}-p_z$ transition bands showed that a heterojunction between the platinum and palladium complexes could be formed in a linear alloy chain. It was revealed that the unit metal-chain length in a one-dimensional alloy could be tuned by the control of the deposited film thickness.

Introduction

There has been increasing interest in a low-dimensional system consisting of not only inorganic materials but also organic compounds because of their peculiar electronic, optical, and magnetic properties.[1−4] It has been known that metal complexes with linear metal chains are one of the most attractive compounds as one-dimensional materials. They have delocalized electrons in the one-dimensional backbone due to strong metal−metal interactions; thus their several electronic properties, such as electron conductivity, have been investigated vigorously.[5−8] Recently, we have suggested that they can also be good candidates for third-order nonlinear optical materials.[9−12] As their electron behaviors are strongly governed by the metal-chain structure, modification of the chain component would greatly contribute to produce unique optoelectronic properties.

It has been generally recognized that alloys often show unique physical and chemical properties that are unexpected in light of their original metals. In this sense, preparation of a one-dimensional alloy consisting of linear metal chains would be quite effective to induce interesting phenomena. Especially, a one-dimensional superlattice consisting of linear metal chains, of which constituents are artificially arranged as designed, might be of particular interest not only for molecular engineering but for also coordination chemistry. Up to the present, there have been several reports for preparing a one-dimensional alloy using metal complexes.[13−19] However, many of these techniques are based on the crystal growth of the metal complex itself. Thus, it seems to be difficult to control the arrangement of constituent metals in a linear chain as designed.

---

† National Institute of Materials and Chemical Research.
‡ The University of Tokyo.
§ Max-Planck-Institut für Festkörperforschung.

(1) Marks, T. J. *Science* **1985**, *227*, 881.
(2) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201.
(3) Graja, A. *Low-Dimensional Organic Conductors*; World Scientific: Singapore, 1992.
(4) Roth, S. *One-Dimensional Metals*; VCH: Weinheim, 1995.
(5) Miller, J. S.; Epstein, A. J. *Prog. Inorg. Chem.* **1976**, *21*, 40.
(6) Tsujikawa, I.; Kubota, R.; Enoki, T.; Miyajima, S.; Kobayashi, H. *J. Phys. Soc. Jpn.* **1977**, *43*, 1459.
(7) Gliemann, G.; Yersin, H. *Struct. Bonding* **1985**, *62*, 87.
(8) Chen, C. T.; Suslick, K. S. *Coord. Chem. Rev.* **1993**, *128*, 293.
(9) Kamata, T.; Fukaya, T.; Mizuno, M.; Matsuda, H.; Mizukami, F. *Chem. Phys. Lett.* **1994**, *221*, 194.
(10) Kamata, T.; Fukaya, T.; Matsuda, H.; Mizukami, F. *Appl Phys. Lett.* **1994**, *65*, 1343.
(11) Kamata, T.; Fukaya, T.; Matsuda, H.; Mizukami, F.; Tachiya, M.; Ishikawa, R.; Uchida, T. *J. Phys. Chem.* **1995**, *99*, 13239.
(12) Kamata, T.; Curran, S.; Roth, S.; Fukaya, T.; Matsuda, H.; Mizukami, F. *Synth. Met.* **1996**, *83*, 267.
(13) Anex, B. G.; Foster, S. I.; Fucaloro, A. F. *Chem. Phys. Lett.* **1973**, *18*, 126.
(14) Holzapfel, W.; Yersin, H.; Gliemann, G. *J. Chem. Phys.* **1981**, *74*, 2124.
(15) Schultheiβ, R.; Hidvegi, I.; Gliemann, G. *J. Chem. Phys.* **1983**, *79*, 4167.
(16) Wang, S.; Garzon, G.; King, C.; Wang, J. C.; Fackler, J. P., Jr. *Inorg. Chem.* **1989**, *28*, 4623.
(17) Takahashi, K.; Tanino, H.; Yao, T. *Thin Solid Films* **1989**, *180*, 173.
(18) Stocks, N. G.; Lambert, C. J.; Mannella, R.; McClintock, P. V. E. *Phys. Rev. B* **1993**, *47*, 8580.
(19) Cordelli, A.; Grosso, G.; Parravicini, G. P. *Phys. Rev. B* **1993**, *48*, 11567.

10.1021/cm990419s CCC: $19.00

It has been known that d^8 transition-metal complexes of dionedioximato have a square−planar configuration and form a one-dimensional structure consisting of linear metal chains.[20,21] They have strong metal−metal interactions and show an absorption band due to the d_{z^2}−p_z transition in the visible region.[22,23] The d_{z^2}−p_z transition band originates from the d-orbital overlap between adjacent metal ions in the linear chain. Thus, the transition is governed by the condition of metal−metal interaction in a linear chain. Electron delocalization in the linear metal chain is due to the d_{z^2}−p_z transition.[24] Furthermore, it has also been known that they can be easily fabricated into a thin film by the conventional vacuum evaporation technique.[25,26] The vapor phase deposition technique has been recognized as one of the most convenient method to control the components in a material. Especially, the highly controlled vacuum evaporation technique, such as a molecular beam epitaxy, is quite useful to control components of a material and has often been used for preparing a superlattice structure.[27,28] Therefore, it seems to be preferable to prepare a one-dimensional alloy using the d^8 transition-metal complexes of dionedioximato.

In a previous paper, we demonstrated that a mixed crystal of bis(dimethylglyoximato)platinum(II)/Pt(dmg)$_2$ and bis(diethylglyoximato)platinum(II)/Pt(deg)$_2$ could be fabricated on a solid substrate by the coevaporation technique.[29] Furthermore, a thin film of Pt(dmg)$_2$ could be prepared on an alkali halide substrate having perpendicular orientation of its linear platinum chain to the surface normal.[30] In this study, we have examined methods for the fabrication of a superstructured one-dimensional alloy in a thin film with the purpose of developing a one-dimensional superlattice whose constituents are arranged as artificially designed by several kinds of metal. A one-dimensional alloy was prepared by coevaporating two different metal complexes with dimethylglyoxime. Control of the chain axis orientation in a thin film was also performed by depositing the metal complexes on several solid substrates. Finally, the one-dimensional superlattice was prepared by depositing several metal complexes one after another.

Experimental Section

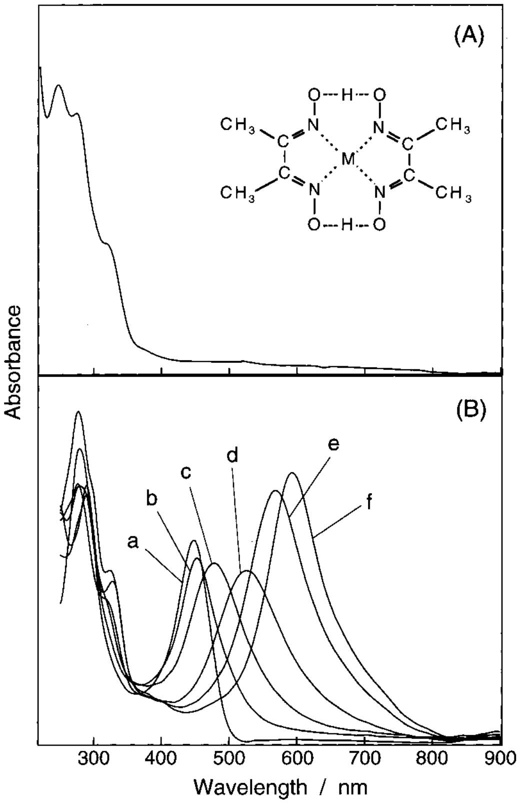

Figure 1. UV−vis absorption spectra of the coevaporated film of Pd(dmg)$_2$ and Pt(dmg)$_2$ deposited on a KBr (100) surface. (A) Spectrum measured by a normal incidence of source light. The fraction of Pt(dmg)$_2$ is 0.39. Inset shows the chemical structure of bis(dimethylglyoximato)metal(II) M(dmg)$_2$ (M = Pd, Pt). (B) Spectra measured by p-polarized source light with incident angle of 70° from the surface normal. The fraction of Pt(dmg)$_2$ is a, 0; b, 0.15; c, 0.39; d, 0.72; e, 0.89; f, 1.0.

The chemical structure of bis(dimethylglyoximato)metal(II) (M(dmg)$_2$, M = Pd, Pt) is shown in Figure 1. M(dmg)$_2$ was prepared by mixing respective hot aqueous−ethanol solutions containing stoichiometric amounts of dimethylglyoxime and high-purity palladium chloride or potassium tetrachloroplatinate(II). Obtained precipitates were collected by filtration, washed with hot water and ethanol, and dried in a vacuum. The final products were purified by repeating recrystallization from the dimethylformamide solution. Pd(dmg)$_2$ formed yellow needlelike crystals. Anal. Calcd for $C_8H_{14}N_4O_4Pd$: C, 28.54; H, 4.19; N, 16.65. Found: C, 28.61; H, 4.19; N, 16.65. Pt(dmg)$_2$ formed dark violet needlelike crystals. Anal. Calcd for $C_8H_{14}N_4O_4Pt$: C, 22.59; H, 3.32; N, 13.18. Found: C, 22.76; H, 3.30; N, 13.01.

Thin films were prepared by conventional vacuum evaporation onto a solid substrate. A KBr single crystal was cleaved just before film deposition, and its (100) surface was used as a substrate. A vacuum chamber was evacuated at 10^{-7} mbar while the substrate was kept at room temperature. In the case of the film preparation of a mixture, two different M(dmg)$_2$ complexes were placed into respective heating boats and simultaneously evaporated onto a KBr-cleaved surface. The initial and residual evaporations were excluded by using an evaporation shutter. The film thickness was monitored by a quartz oscillator (INFICON model XTM/2). The evaporation rate was ca. 0.6 nm/min. The elemental composition of the film was estimated by X-ray photoelectron spectroscopy using a Perkin-Elmer Phi5600 XPS system. The transmission absorption spectra of obtained films were recorded on a Shimadzu UV-3100 spectrophotometer in the wavelength range between 200 and 1000 nm. To estimate a perpendicular orientation of a transition moment for an absorption band, the absorption transmission spectrum was measured with a p-polarized source light through a Glan−Thompson prism whose incident angle was 70° from the surface normal. X-ray diffraction patterns were obtained by a Mac Science MXP-18 diffracto-

---

(20) Thomas, T. W.; Underhill, A. E. *Chem. Soc. Rev.* **1972**, *1*, 99.

(21) Endres, H.; Keller, H. J.; Lehmann, R.; Poveda, A.; Rupp, H. H.; Sand, H. V. D. *Z. Naturforsch* **1977**, *32*, 516.

(22) Ohashi, Y.; Hanazaki, I.; Nagakura, S. *Inorg. Chem.* **1970**, *9*, 2551.

(23) Anex, B. G.; Krist, F. K. *J. Am. Chem. Soc.* **1967**, *89*, 6114.

(24) Yamamoto, K.; Kamata, T.; Iwai, S.; Kazaoui, S.; Minami, N.; Mizukami, F.; Misawa, K.; Ohta, T.; Kobayashi, T. *Chem. Phys. Lett.* **1999**, *302*, 609.

(25) Shirotani, I.; Suzuki, K.; Suzuki, T.; Yagi, T.; Tanaka, M. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1078.

(26) Isoda, S.; Tsujimoto, M.; Yoshida, K.; Ogawa, T.; Kobayashi, T.; Kamata, T. *Mol. Crys. Liq. Crys.* **1998**, *316*, 71.

(27) Yoshimura, T.; Tatsuura, S.; Sotoyama, W. *Appl. Phys. Lett.* **1991**, *59*, 482.

(28) Imanishi, Y.; Hattori, S.; Kakuta, A.; Numata, S. *Phys. Rev. Lett.* **1993**, *71*, 2098.

(29) Yamamoto, K.; Kamata, T.; Yoshida, Y.; Yase, K.; Fukaya, T.; Mizukami, F.; Ohta, T. *Chem. Mater.* **1998**, *10*, 1343.

(30) Yamamoto, K.; Kamata, T.; Yoshida, Y.; Yase, K.; Mizukami, F.; Ohta, T. *Adv. Mater.* **1998**, *10*, 1018.

meter with the use of Cu Kα radiation (1.5405 Å). Reflections were recorded over the range of 2θ ($3° < 2\theta < 50°$) in approximately 20 min.

Results and Discussion

Mixed Crystal with a Linear Alloy Chain. The preparation of a superlattice structure with a one-dimensional system was examined using d^8 transition-metal complexes with dionedioxime. To fabricate such a one-dimensional superlattice, it would be required that two different metal–dionedioxime complexes form a mixed crystal with a linear metal chain whose axes grow along the surface normal in the deposited film. In a previous study,[29] we demonstrated that Pt(dmg)$_2$ formed a mixed crystal with bis(diethylglyoximato)-platinum(II) Pt(deg)$_2$ on a glass substrate by the coevaporation technique. Furthermore, it was revealed that Pt(dmg)$_2$ deposited on an alkali halide-cleaved surface showed a perpendicular orientation of its linear chain axis to the film surface.[30] A similar perpendicular orientation was also reported for the bis(1,2-benzoquinonedioximato)platinum(II) thin film.[31] Then, a mixture of Pd(dmg)$_2$ and Pt(dmg)$_2$ was deposited on a cleaved KBr (100) surface by the coevaporation technique, and its film structure was examined.

The mixture of Pd(dmg)$_2$ and Pt(dmg)$_2$ with several compositions was fabricated into a thin film on a KBr-cleaved surface by coevaporation. Figure 1A shows the UV–vis absorption spectra of the coevaporated film of the mixture with the Pt(dmg)$_2$ fraction of 0.39. The spectra were measured with a normal incident light source. Strong absorption bands appeared at 244, 278, and 322 nm. These are assigned to the $\pi-\pi^*$ transition bands of Pd(dmg)$_2$ and Pt(dmg)$_2$ and the metal–ligand charge-transfer transition bands of Pt(dmg)$_2$, respectively. The metal–ligand charge-transfer transition band of Pd(dmg)$_2$ seems to be on the shoulder of the strong 278 nm band. Normally, it has been known that M(dmg)$_2$ shows three strong absorption bands, namely, the $\pi-\pi^*$ transition, the metal–ligand charge-transfer transition, and the $d_{z^2}-p_z$ transition bands. However, the $d_{z^2}-p_z$ transition band could not be observed in the spectrum. Disappearance of the band was common for all prepared films including the original precursor M(dmg)$_2$ films. The $d_{z^2}-p_z$ transition band is known to originate from the d-orbital overlap between the adjacent metal ions in the linear metal chain; therefore, it is strongly affected by intermolecular interaction.[22,23] If molecules have metal–metal interactions, the band should appear in the visible region. While the transition moments of the $\pi-\pi^*$ and metal–ligand charge-transfer transitions are perpendicular to the chain axis, that of the $d_{z^2}-p_z$ transition band is parallel to the chain axis. To study the orientational effect, an oblique incident transmission absorption spectrum for the film deposited on a KBr substrate was also measured using a p-polarized source light with an incident angle of 70° from the surface normal. Figure 1B shows the UV–vis spectra of the films. These spectra are quite reproducible. The $d_{z^2}-p_z$ transition band could be observed at 443 nm for pure Pd(dmg)$_2$ and 599 nm for pure Pt(dmg)$_2$, respectively. Therefore, disappearance of the $d_{z^2}-p_z$ transition band in Figure 1A can be attributed to the orientational effect of the band.

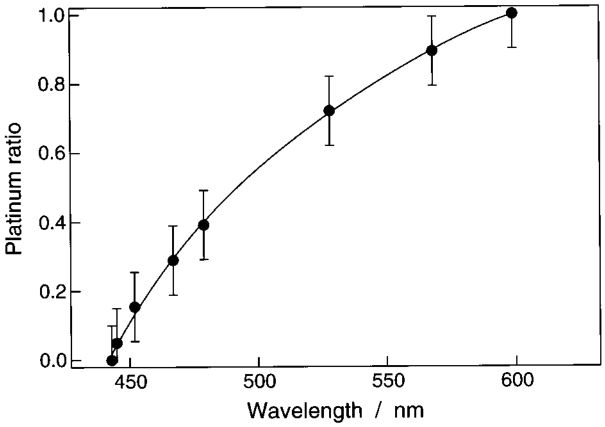

Figure 2. Peak wavelengths of the $d_{z^2}-p_z$ transition band of the coevaporated film of Pd(dmg)$_2$ and Pt(dmg)$_2$ plotted against the fraction of Pt(dmg)$_2$.

The peak wavelength of the $d_{z^2}-p_z$ transition band for the mixture was subsequently shifted in proportion to the metal composition. Figure 2 shows peak wavelengths of the $d_{z^2}-p_z$ transition band plotted against the fraction of Pt(dmg)$_2$. If both precursor metal complexes are independently crystallized in a deposited film, the $d_{z^2}-p_z$ transition bands should appear independently at their original peak wavelength. The $d_{z^2}-p_z$ transition band is greatly affected by intermolecular interaction; thus its peak wavelength is governed by the types of metal–metal interactions that occur in the linear chain. The appearance of a new strong band in the visible region for the film of the mixture, which was different from the $d_{z^2}-p_z$ transition bands of their pure M(dmg)$_2$ complexes, indicates that another metal–metal interaction occurs in the deposited film. On the other hand, both the $\pi-\pi^*$ and metal–ligand charge-transfer transition bands could be observed at almost the same wavelength as those of the pure M(dmg)$_2$ in any spectra of the mixtures. Their peak intensities were dependent upon the mixing ratio. These $\pi-\pi^*$ and metal–ligand charge-transfer transition bands of Pd(dmg)$_2$ increased in intensity with an increase in the palladium content, and the bands of Pt(dmg)$_2$ increased with an increase in the platinum content. As the $\pi-\pi^*$ and metal–ligand charge-transfer transitions are intramolecular transitions and less sensitive to the intermolecular interaction, it is natural that their peak wavelengths were almost independent of the metal complex mixing. Their peak intensities simply reflected the composition of respective metal complexes in the film.

X-ray diffraction patterns were also measured for respective sample films. Figure 3 shows the X-ray diffraction patterns of the thin films of pure Pd(dmg)$_2$, Pt(dmg)$_2$, and their mixture deposited on a quartz substrate. Sharp diffraction lines are observed at $2\theta =$ 9.90, 19.86, 30.02, and 40.34° for a pure Pd(dmg)$_2$ film and at 9.88, 19.85, 29.98, and 40.28° for a pure Pt(dmg)$_2$ film. It has been known that M(dmg)$_2$ crystallizes in the orthorhombic system with the unit cell constants shown in Table 1.[32,33] The obtained diffraction lines are com-

---

(31) Shirotani, I.; Minobu, N.; Ohtsuki, Y.; Yamochi, H.; Saito, G. *Chem. Phys. Lett.* **1988**, *147*, 231.

(32) Godycki, L. E.; Rundle, R. E. *Acta Crystallogr.* **1953**, *6*, 487.

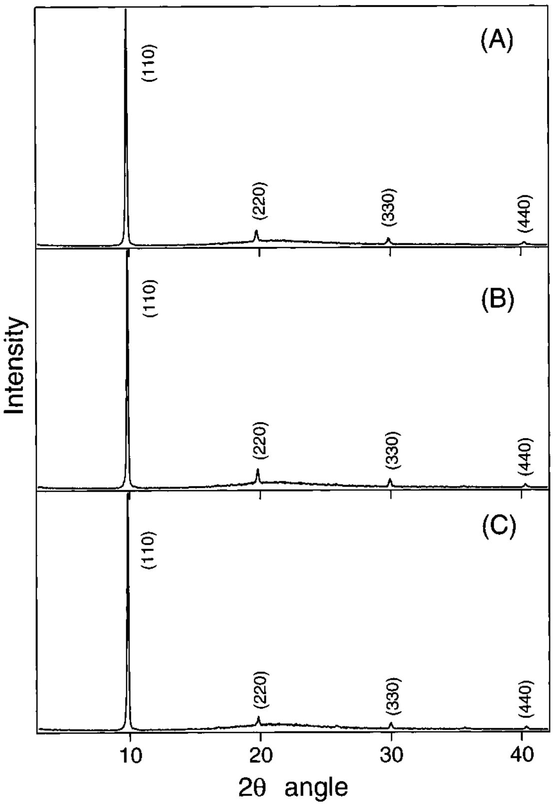

Figure 3. X-ray diffraction patterns of the films of (A) Pd(dmg)$_2$, (B) Pt(dmg)$_2$, and (C) mixture of Pd(dmg)$_2$ and Pt(dmg)$_2$ deposited on a quartz substrate.

Table 1. Unit Cell Constants of Ni(dmg)$_2$,[32] Pd(dmg)$_2$,[33] and Pt(dmg)$_2$[33]

	Ni(dmg)$_2$	Pd(dmg)$_2$	Pt(dmg)$_2$
a (Å)	16.68	16.76	16.82
b (Å)	10.44	10.50	10.56
c (Å)	6.49	6.50	6.51
M−*M* (Å)	3.25	3.25	3.25
Z	4	4	4
space group	*ibam*	*ibam*	*ibam*
D_c (g/cm^3)	1.61	1.98	2.46
crystal system	orthorhombic	orthorhombic	orthorhombic

posed of (110), (220), (330), and (440) reflections for both Pd(dmg)$_2$ and Pt(dmg)$_2$. As their unit cell constants are almost the same to each other, 2θ angles of (*nn*0) reflections of the Pt(dmg)$_2$ film are very close to those of the Pd(dmg)$_2$ film. Appearance of sharp and strong (*nn*0) reflections indicates that the M(dmg)$_2$ molecules are highly ordered on a quartz substrate and mainly arranged as the stacking axes (*c*-axis) are parallel to the substrate surface. The X-ray diffraction pattern of Pd(dmg)$_2$−Pt(dmg)$_2$ mixture with 3:2 mixing ratio is also shown in Figure 3. Sharp and strong diffraction lines are observed at $2\theta = 9.90$, 19.86, 30.02, and 40.30°. This diffraction pattern is almost the same as those of pure M(dmg)$_2$. This means that the mixture is crystallized and highly ordered in the deposited film. Their stacking arrangement in the film seems to be almost the same as that of pure M(dmg)$_2$, although the linear metal chain contains heterometals.

Figure 4 shows X-ray diffraction patterns of thin films of Pd(dmg)$_2$, Pt(dmg)$_2$, and their 3:2 mixture deposited on a KBr (100) surface. The diffraction patterns are entirely different from those observed for the same film deposited on a quartz substrate (Figure 3). The (*nn*0) reflections, which appeared strongly for the film deposited on a quartz substrate, could not be observed on a KBr (100) surface. In place of them, sharp diffraction lines appeared at $2\theta = 27.06$ and 27.36° for the pure Pd(dmg)$_2$ film and at 27.02 and 27.44° for the pure Pt(dmg)$_2$ film. The diffraction lines around 27.0° are assigned to the (200) reflection of the KBr substrate. Diffraction lines at 27.36 and 27.44° are composed of the (002) reflection of Pd(dmg)$_2$ and Pt(dmg)$_2$, respectively. This indicates that the M(dmg)$_2$ molecules are arranged with their stacking axes perpendicular to the substrate surface. In the X-ray diffraction pattern of the mixture, a sharp diffraction line was also observed at $2\theta = 27.38°$ besides the diffraction line of 27.02° due to the KBr (200) reflection. The diffraction line at 27.38° corresponds to a *d* spacing of 0.325 nm that is almost the same as those of the (002) reflections of Pd(dmg)$_2$ and Pt(dmg)$_2$. As described above, the mixture has almost the same crystal structure as Pd(dmg)$_2$ and Pt(dmg)$_2$. Thus, it can be concluded that the diffraction line at 27.38° is assigned to the (002) reflection of the mixture and the alloy chain axes are perpendicularly oriented to the substrate surface. These results are very consistent with those obtained from the UV−vis absorption spectra; the linear alloy chain is highly ordered with its axis perpendicular to the film plane in a deposited thin film. The X-ray diffraction patterns were almost independent of metal mixing. This indicates that the crystal structure of M(dmg)$_2$ is almost independent of the metal constituents that form linear metal chains.

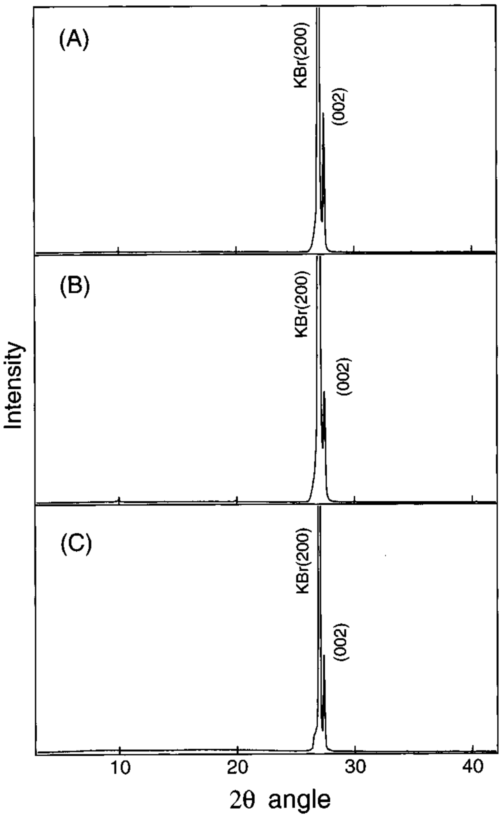

Figure 4. X-ray diffraction patterns for the deposited thin film of (A) Pd(dmg)$_2$, (B) Pt(dmg)$_2$, and (C) mixture of Pd(dmg)$_2$ and Pt(dmg)$_2$ on a KBr (100) surface.

---

(33) Hussain, M. S.; Salinas, B. E. V.; Schlemper, E. O. *Acta Crystallogr.* **1979**, *B35*, 628.

Observed results indicate that coevaporation of two different metal complexes with dimethylglyoxime gives a thin film consisting of their mixture in which linear chains are composed of heterometal ions, namely a one-dimensional alloy. Even though the linear metal chain contains about 5% heterometal, a peak shift of the d_{z^2}–p_z transition band could be observed. This means that only delocalized electrons are extended over a relatively long distance in the linear metal chain. Their chain axes are perpendicularly oriented to the film surface on the KBr-cleaved surface. As the lattice constants are scarcely different among the nickel, palladium, and platinum complexes and close to each other, they crystallize in almost the same unit cell (Table 1). This must be closely related to the fact that metals in linear metal chains are easily replaced by another metal, which results in the formation of linear alloy-chains.

Fabrication of a One-Dimensional Superlattice. In the section above, we have demonstrated that two different metal complexes with dimethylglyoxime form a one-dimensional alloy chain in a coevaporated film, and the chain axis in a film deposited on a cleaved KBr (100) surface grows along the surface normal. These results would make it possible to prepare a superstructured one-dimensional alloy that is composed of several kinds of unit metal chains. The unit metal-chain length would be defined by the deposited film thickness. Here, $Pd(dmg)_2$ and $Pt(dmg)_2$ films were deposited on a cleaved KBr surface alternately to prepare a one-dimensional superlattice.

To prepare a superstructured one-dimensional alloy film, $Pt(dmg)_2$ film was deposited as the first layer with a certain unit thickness on a cleaved KBr (100) surface. Subsequently, $Pd(dmg)_2$ film was deposited with the same unit thickness on the first $Pt(dmg)_2$ layer. This alternative deposition cycle was repeated to give a total film thickness of ca. 80 nm. Each deposition was carried out with a deposition rate of 0.6 nm/min at intervals of 5 min. Figure 5 shows the absorption spectra of the alternatively deposited films measured with a normal and oblique incidence of source light. Film A was prepared by a single alternative deposition cycle of $Pt(dmg)_2$ and $Pd(dmg)_2$ with a respective unit layer thickness of 40 nm. It gave strong absorption bands at 244, 278, and 322 nm in the spectrum measured by a normal incidence of source light. Those are assigned to the π–π^* transition bands of $Pd(dmg)_2$ and $Pt(dmg)_2$ and the metal–ligand charge-transfer transition bands of $Pt(dmg)_2$, respectively. The d_{z^2}–p_z transition bands of both $M(dmg)_2$ could not be observed. On the other hand, in the spectrum measured by an oblique incidence of source light for the same film, the d_{z^2}–p_z transition bands could be observed clearly and independently at 442 and 599 nm. These correspond well to those of the pure $Pd(dmg)_2$ and $Pt(dmg)_2$, respectively. The X-ray diffraction pattern of the prepared film was almost the same as that of their pure films deposited on a KBr substrate. Namely, a sharp (002) diffraction line could be observed. This indicates that $Pd(dmg)_2$ and $Pt(dmg)_2$ are not mingled in the deposited film such as in a mixed crystal and that both metal-chain axes are independently well-oriented perpendicular to the film surface.

The peak wavelength of the π–π^* and metal–ligand charge-transfer transitions were almost independent of the unit layer thickness. However, the peak wavelengths of the d_{z^2}–p_z transition band were altered with the unit layer thickness. For example, film D, which was prepared by 16 cycles of alternate deposition with a respective unit layer thickness of 2.5 nm, showed the π–π^* and metal–ligand charge-transfer transition bands at 245, 280, and 320 nm and the d_{z^2}–p_z transition band at 451 and 560 nm. The d_{z^2}–p_z transition band, due to the palladium chain, appeared at a longer wavelength and that of the platinum chain at a shorter wavelength than those of the pure $M(dmg)_2$ films. The X-ray diffraction pattern of the film was almost the same as those for the other prepared films, indicating that the chain axis orientation was kept perpendicular to the film surface even though the alternative deposition cycle was repeated 16 times. The d_{z^2}–p_z transition peak wavelengths were plotted against the unit layer thickness in Figure 6. The d_{z^2}–p_z transition peak wavelength due to the palladium chain showed a redshift and that of the platinum chain showed a blueshift with decreasing unit layer thickness. If both metal chains were isolated completely without platinum–palladium interaction in the film, the peak wavelengths should be simply reflective of a small domain size of a metal chain. In such a case, the peak wavelengths of both metals seem to show the same tendency, such as a blueshift or

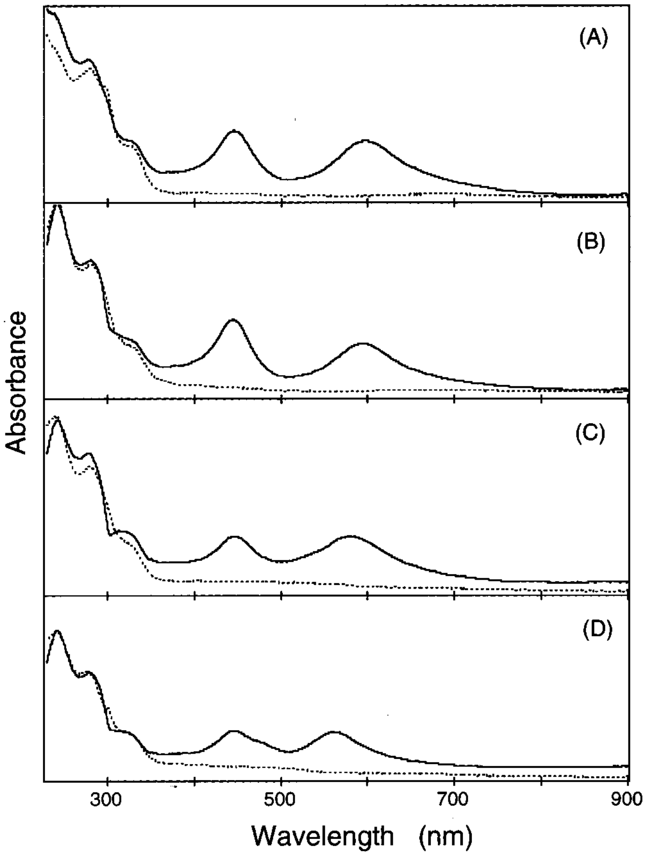

Figure 5. UV–vis absorption spectra of the film prepared by alternate deposition of $Pt(dmg)_2$ and $Pd(dmg)_2$ on a cleaved KBr (100) surface. Films prepared with (A) 1 cycle of alternative deposition with a respective unit layer thickness of 40 nm, (B) 2 cycles with a unit layer thickness of 20 nm. (C) 8 cycles with a unit layer thickness of 5 nm. (D) 16 cycles with a respective unit layer thickness of 2.5 nm. Dotted line: spectra measured by normal incident light source. Solid line: spectra measured by p-polarized source light with incident angle of 70° from the surface normal.

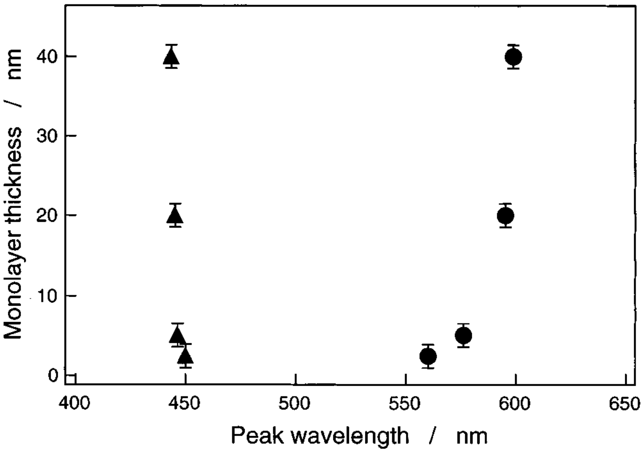

Figure 6. Peak wavelengths of the $d_{z^2}-p_z$ transition band of (▲) palladium and (●) platinum chains in the alternatively deposited film of Pd(dmg)$_2$ and Pt(dmg)$_2$ plotted against the unit layer thickness.

disappearance. However, observed peak shifts were quite similar to those of metal-chain mixing, as shown in the former section. In the platinum chain, the peak wavelength shifted to shorter wavelengths with increasing palladium content. In the palladium chain, it shifted to longer wavelengths with increasing platinum content. These peak shifts apparently originated in the palladium−platinum interaction in an alloy chain. Therefore, the observed results for the alternately deposited film indicate that there are heterojunctions between the platinum and palladium in a linear chain in the alternately deposited film and that the unit length of a metal chain in the one-dimensional alloy was defined by its deposited layer thickness. This can be recognized as a superstructured one-dimensional alloy.

As the metal−metal distance of Pd(dmg)$_2$ and Pt(dmg)$_2$ is 0.325 nm in both, the unit film thickness of 2.5 nm for the film D corresponds to the unit metal chain composed of 7.7 metals. The film D showed absorption peaks of the $d_{z^2}-p_z$ transition band at 451 nm for the palladium chain and 560 nm for the platinum chain. Here, we considered that the observed peak shifts for the alternately deposited film are attributed to the hetero-interaction between platinum and palladium in a linear chain similar to the mixed crystal. In Figure 2, 451 nm of the $d_{z^2}-p_z$ transition band corresponded to that of the 8:1 mixture of Pd(dmg)$_2$ and Pt(dmg)$_2$, and 560 nm to that of the 1:6 mixture. This means that the average chain length of a metal is 8 for palladium and 6 for platinum. These metal-chain lengths correspond well to the average metal-chain number estimated from the film thickness within the experimental error. Namely, the alloy chain was composed of about a 7-metal-chain unit, and respective chain units interacted with each other at heterojunctions between platinum and palladium in a linear alloy chain.

In the above discussion, each unit layer is considered to have an atomically flat surface. However, we have reported that the Pt(dmg)$_2$ film grows in island shapes on the KBr-cleaved surface in a previous paper.[30] Even though each layer was deposited very carefully, it seems to be difficult to obtain perfectly flat atomic layers of these metal complexes. Therefore, the film thickness can only be controlled as an average value with some distribution. Despite such a finding, obtained results indicated that respective unit chain components were controlled to have a certain length and showed unique optical properties, i.e., two different types of peak shift. These phenomena may be obtained in a small domain level. Optical properties are fundamentally observed as average properties of the prepared sample. Therefore, they would be enough to investigate their linear or nonlinear optical properties that are originated from the low-dimensional quantum effects peculiar to the superlattice structure.

Conclusions

In this study, we have fabricated a mixed crystal with linear alloy chains by simultaneous vacuum evaporation of two different metal complexes with dimethylglyoxime. These mixed crystals showed a strong $d_{z^2}-p_z$ transition band in the visible region whose peak wavelength subsequently varied in proportion to the mixing ratio. In contrast to these spectral changes, no distinct difference could be observed in the X-ray diffraction patterns among mixtures. Theses results indicate that alloying of the metal chain would make it possible to tune the strong $d_{z^2}-p_z$ transition wavelength between those of pure metal complexes without any drastic structural changes.

We have also succeeded in obtaining a perpendicular orientation of the alloy chain axis to the surface by depositing the mixed crystal on a KBr-cleaved surface. It is desirable to fabricate a one-dimensional superlattice in which several metal components are artificially arranged in a linear chain because a one-dimensional superlattice can be prepared by depositing several metal complexes one after another and its unit length can be defined by the deposited film thickness.

Finally, we have demonstrated a method to fabricate a superstructured one-dimensional alloy that is composed of periodic unit platinum and palladium chains with a limited length. A well-known superlattice consists of highly controlled layered structures and, thus, has a well-defined two-dimensional system. The demonstrated one-dimensional superlattice is composed of alloy wires in which several metals are purposefully arranged. These one-dimensional superlattices would give interesting and unique optoelectronic phenomena, such as the one-dimensional to zero-dimensional transition of the quantum confinement effects.

Acknowledgment. T.K. acknowledges financial support from the Alexander von Humboldt Foundation.

CM990419S