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Molecular Precursor Method for Fabricating *p*-Type Cu₂O and Metallic Cu Thin Films

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Abstract

Functional thin films are used in various fields of our life. Many different methods are used to fabricate these films including physical vapor deposition (PVD) and chemical processes. The chemical processes can be used to manufacture thin films in a relatively cheap way, as compared to PVD methods. This chapter summarizes the procedures of the molecular precursor method (MPM), a chemical process, for fabrication of both metal oxide semiconductor Cu₂O and metallic Cu thin films by utilizing Cu(II) complexes in coating solutions. The MPM, recently developed and reported by the present authors, represents a facile procedure for thin film fabrication of various metal oxides or phosphates. This method pertinent to the coordination chemistry and materials science including nanoscience and nanotechnology has provided various thin films of high quality. The MPM is based on the design of metal complexes in coating solutions with excellent stability, homogeneity, miscibility, coatability, etc., which are practical advantages. The metal oxides and phosphates are useful as the electron and/or ion conductors, semiconductors, dielectric materials, etc. This chapter will describe the principle and recent achievement, mainly on fabricating the *p*-type Cu₂O and metallic Cu thin films of the MPM.

Keywords: molecular precursor method, thin film, *p*-type Cu₂O, copper

1. Introduction

A sustainable society requires innovative technology where many disciplines interact. Highly functionalized thin films in various devices such as computers, which were developed mainly for the semiconductor industry in the last century, are now widely used in various fields of our daily life. For example, the touch panel in mobile phone uses a transparent conductive thin film and an antireflection thin film on the glass. A product with various thin films makes

life more comfortable. Many different methods are used to fabricate such thin films including physical vapor deposition (PVD) such as laser ablation, molecular beam epitaxy, sputtering, and chemical processes [1]. The chemical processes can be used to manufacture thin films in a relatively cheap way compared to PVD methods. The chemical process is a processing technique for preparing thin films, ceramic coatings, and powders. However, it is usually difficult to fabricate high-quality thin films using chemical processes.

Transparent metal oxide thin films of *p*-type semiconductors deposited directly on various substrates offer several advantages in the design of heterojunctions with *n*-type oxide films for fabricating thin film devices [2, 3]. Over the past years, the quest to obtain high-quality cuprous oxide films has fueled the development of many physical processing techniques including sputtering, thermal oxidation, vacuum evaporation, molecular beam epitaxy, and electrodeposition [4–9]. However, reproducible formation of cuprous oxide films, uncontaminated by copper or the CuO phase, is a formidable challenge from the technical perspective. Most of the aforementioned physical processing techniques are not economically viable in large area applications. The chemical procedures, which save both energy and resources, have therefore emerged as an attractive alternative because of cost-effective production capabilities.

Recently, we achieved the fabrication of *p*-type Cu₂O transparent thin films by means of a chemical process, the molecular precursor method (MPM), using the thermal reaction of molecular precursor films spin-coated on a Na-free glass substrate. A stable precursor solution for the spin-coating process was facilely prepared by reacting an isolated Cu(II) complex of ethylenediamine-*N*, *N*, *N*', *N*'-tetraacetic acid (EDTA, H₄edta) with dibutylamine in ethanol [10, 11]. The MPM is one of the chemical processes used for thin film formation of metal oxides or phosphates [12–22]. The method is based on the formation of excellent precursor films involving anionic metal complexes and the alkylammonium cation. The stability, homogeneity, miscibility, and other characteristics of the precursor solutions, which can be used for various coating methods, are practical advantages, in contrast to the conventional sol-gel method.

This chapter summarizes the procedures used in the MPM for the fabrication of both metal oxide semiconductor Cu₂O and metallic Cu thin films by utilizing Cu(II) complexes in coating solutions.

2. Molecular precursor method

The decision by the Nobel Prize committee to award the Nobel Prize for chemistry in 1913 to Alfred Werner met with worldwide approval. In a statement, the committee said that Alfred Werner received the prize in recognition of his work on the linkage of atoms in molecules by which he has thrown new light on earlier investigations and opened up new fields of research especially in inorganic chemistry [23]. Today, the metal complexes are used in various applications such as catalysts, luminescence, and medicine. In 1996, one of the authors, M.S., focused on the thin film fabrication of various metal oxides and phosphate compounds

using the metal complexes of stable [10–22]. This is the MPM, which is one of the chemical processes used for thin film fabrication. In those days, most of the researchers in the field of thin film formation by chemical processes preferred to use rather unstable metal complexes. It is easy to imagine the capability of polymers to form films because we use polymer films every day. In fact, well-adhered precursor films can be formed on various substrates by coating the solution dispersing the produced oligomers and polymers including metallic species provided by hydrolyzing the unstable metal complexes. These results led us to believe for a long time that only the oligomers and polymers can form precursor films, but the stable metal complexes having discrete molecular weight would not be useful in the formation of such thin films. The MPM was a challenge to this central belief.

The MPM, pertinent to coordination chemistry and materials science including nanoscience and nanotechnology, has been used to fabricate various high-quality thin films with appropriate film thicknesses. As a result, the MPM represents a facile procedure for thin film fabrication of various metal oxides or phosphates, which are useful as electron and/or ion conductors, semiconductors, dielectric materials, etc [24, 25].

Figure 1 shows the Co₃O₄ thin films, which were first fabricated using the molecular precursor solutions. To date, more than 40 kinds of metal oxides or phosphates have been easily fabricated. **Figure 2** shows the general protocol for fabricating the titanium dioxide thin films. First, a water-resistant coating solution was prepared by the reaction of a neutral [Ti(H₂O)(edta)] complex with dipropylamine in ethanol, where edta represents ethylenediamine-*N, N, N', N'*-tetraacetate anion. Molecular precursor solutions can be used in spin, dip, or spray coating on various material surfaces to form precursor thin films. To obtain the precursor film, the coated film was dried at around 70°C. The precursor films involving metal complexes should be amorphous, just as with the metal/organic polymers in the sol-gel processes; otherwise, it would not be possible to obtain the resulting metal oxide thin films spread homogeneously on substrates by using the following heat treatment. After this, the precursor film was heat-treated at appropriate temperatures for eliminating the components in the organic ligand from the metal complexes involved in the precursor films and to fabricate thin films of crystallized metal oxides or phosphates. The heat treatment of a well-adhered precursor film at 450°C in air is useful for the fabrication of transparent titania thin films.



Figure 1. The Co₃O₄ thin films which were first time to fabricate the thin film using the molecular precursor solutions.

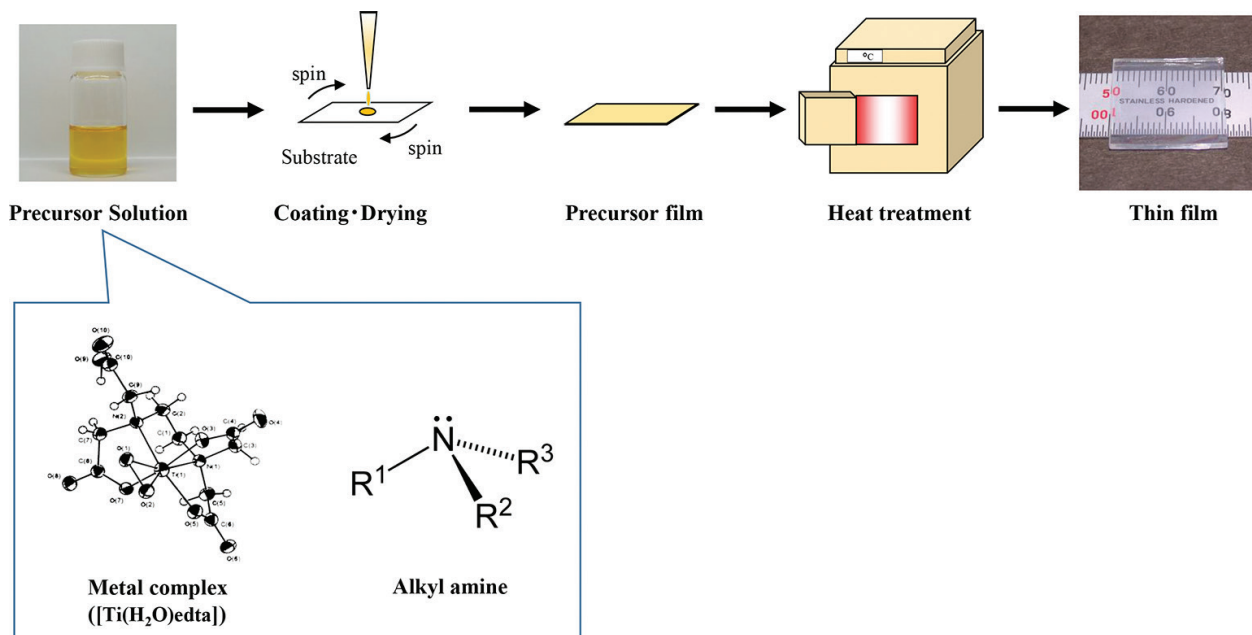


Figure 2. Protocol for fabricating the thin film using the molecular precursor method.

Cuprous oxide, Cu_2O , with a cubic structure is a potential candidate for *p*-type semiconductors having a band gap of 2.0 eV, which is the band gap of its single crystal. The thin films of Cu_2O can be grown generally by dry processes in a vacuum chamber at high temperature, such as sputtering, thermal oxidation, and pulsed laser deposition [26–28]. Over the past years, the quest to obtain high-quality Cu_2O films has fueled the development of many physical processing techniques including sputtering, thermal oxidation, vacuum evaporation, molecular beam epitaxy, and electrodeposition. However, reproducible formation of Cu_2O films uncontaminated by the CuO phase is a formidable challenge from the technical perspective [29, 30]. In addition, most of the aforementioned physical processing techniques are not economically viable in large area applications. Solution-based processes have, therefore, emerged as attractive alternatives because of the ability for cost-effective production [31]. Armelao and coworkers have successfully employed a sol-gel solution containing dissolved copper acetate to produce a Cu_2O thin film [32]. The semiconductive nature of the thin film was, however, unclear owing to the lack of Hall effect measurements in their work.

Recently, *p*-type Cu_2O transparent thin films were fabricated using the thermal reaction of molecular precursor films spin-coated on a Na-free glass substrate [10]. A stable precursor solution for the spin-coating process was readily prepared by reacting an isolated Cu(II) complex of EDTA with dibutylamine in ethanol. The 50-nm-thick Cu_2O thin film resulting from heat treatment of the precursor film at 450°C for 10 min in Ar gas at a flow rate of 1.0 L min^{-1} was characterized by X-ray diffraction (XRD). **Figure 3** shows the XRD pattern of the resultant thin film deposited on the Na-free glass substrate after heat treating the precursor film. The XRD pattern of the resultant thin film indicated a precise cubic lattice cell parameter with $a = 0.4265(2) \text{ nm}$, with a crystallite size of $8(2) \text{ nm}$. No additional peaks from any possible contaminants such as Cu and CuO appeared in the XRD pattern of the Cu_2O film. X-ray

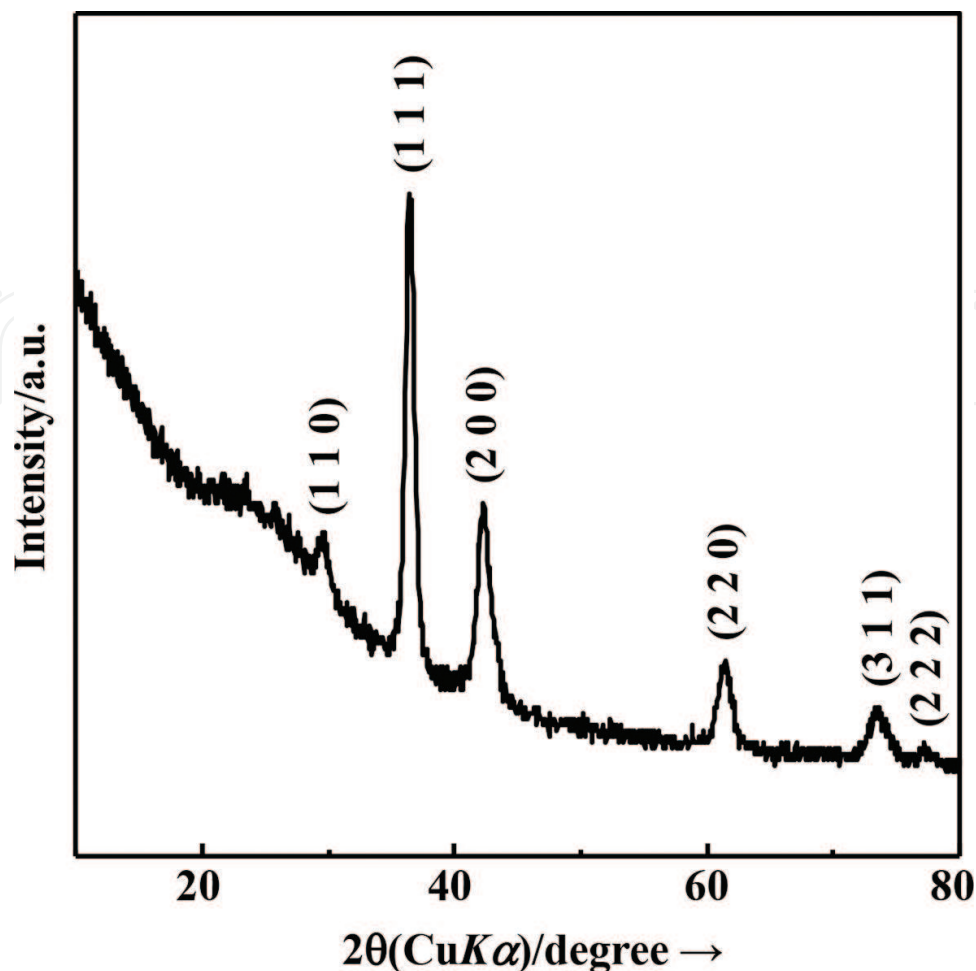


Figure 3. XRD pattern of the thin film adhered to a Na-free glass substrate after heat treatment at 450°C for 10 min in Ar gas at a flow rate of 1.0 L min⁻¹.

photoelectron spectroscopy (XPS) peaks attributed to the O 1s and Cu 2p_{3/2} level of the Cu₂O film were observed at 532.6 and 932.4 eV, respectively. The peak position of the Cu 2p_{3/2} level is identical to the reported values, which were observed for Cu₂O thin films prepared by other methods [31, 33]. In addition, no peak for the CuO phase was observed at its typical value of 944 eV [31]. The average grain size of the deposited Cu₂O particles was ~200 nm, observed via field-emission scanning electron microscopy (FE-SEM). The optical band edge evaluated from the absorption spectrum of the transparent Cu₂O thin film was 2.3 eV, assuming a direct transition semiconductor. The tensile strength of the films on the glass substrate was measured by a stud pull adhesion test. The tensile strength of the adhesion of the Cu₂O thin film to the substrate was 83(2) MPa, indicating strong adhesion to the glass substrate.

Figure 4 shows the Arrhenius plot of the Cu₂O thin film on the Na-free glass substrate over the temperature range 160–300 K. Hall effect measurements of the thin film indicated that the single phase Cu₂O thin film is a typical *p*-type semiconductor with a hole concentration of 1.7 × 10¹⁶ cm⁻³ and hole mobility of 4.8 cm² V⁻¹ s⁻¹ at ambient temperature. The activation energy from the valence band to the acceptor level was determined as 0.30 eV by least-square fitting using the free carrier concentration spectroscopy (FCCS) method [34].

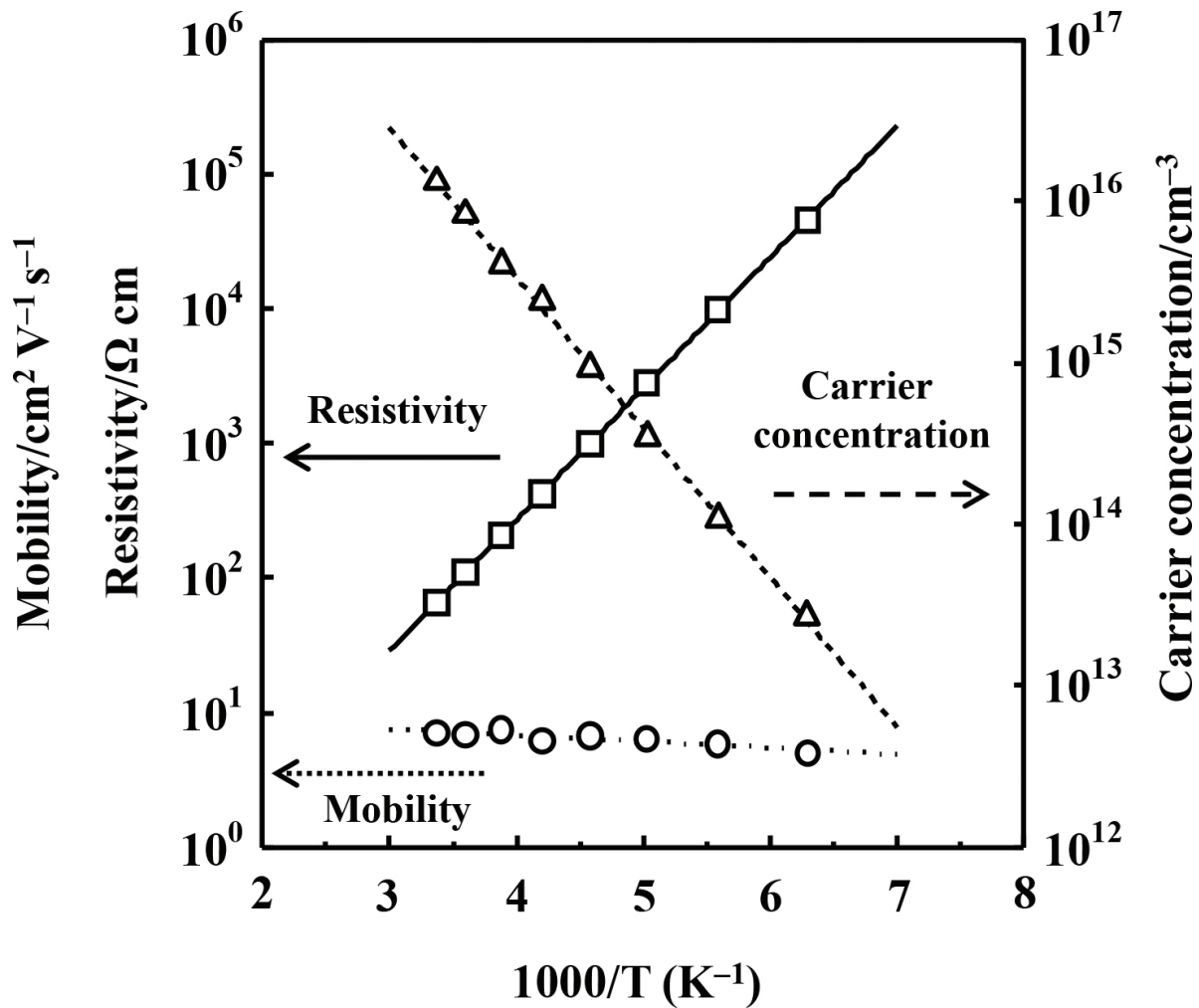


Figure 4. Temperature dependency of the resistivity (—◇—), carrier mobility (...○...), and carrier concentration (...△...) of the thin film. Film was formed by heat treatment at 450°C for 10 min in Ar gas at a flow rate of 1.0 L min⁻¹ on a 10 × 10 × 1.1 mm³ Na-free glass substrate.

The resistivity of the Cu₂O thin film fabricated using the MPM was lower than that of both films obtained by the oxidation of a copper film and by the dc reactive magnetron sputtering process [26–28]. It was observed that the carrier concentration tends to be high and the carrier mobility is low for the Cu₂O thin film fabricated by the MPM, compared to the thin films formed by previously reported processes (Table 1).

The method described is the first example of fabrication and characterization of *p*-type Cu₂O transparent thin films using a coating solution prepared from a starting Cu²⁺ complex of the H₂edta²⁻ ligand. Reduction of the Cu²⁺ species occurred unambiguously through the heating process under Ar gas flow. The CuO phase could be found in the thin film by the prolonged reactions after fabricating the Cu₂O thin film at the identical atmospheric condition and temperature. This result indicates that the formation mechanism of Cu₂O in the MPM differs from that of the sol-gel method, in which the Cu₂O phase was derived from the CuO phase in N₂ atmosphere at 90°C. It is notable that the quality of the resultant thin film fabricated

Method	Annealing condition			Thickness nm	Carrier concentration (cm ⁻³)	Mobility (cm ² V ⁻¹ s ⁻¹)	Resistivity Ω cm
	Temperature	Atmosphere	Time				
Molecular precursor method	450	Ar gas flow	10 min	50	4.8	76	4.8
Oxidation method [26]	400	10% O ₂ in Ar gas	5 min	230	6.1	370	6.1
Magnetron sputtering [27]	200	O ₂ gas pressure of 1.1 × 10 ⁻³ torr in vacuum	–	130	0.36	1.8	0.36
Pulsed laser deposition [28]	500	In vacuum	6 h	100	32	100	32

Table 1. Comparison of electrical properties of the thin film fabricated herein using a 0.3 mmol g⁻¹ precursor solution under Ar gas at a flow rate of 1.0 L min⁻¹, versus those of the films formed by other methods. All values were measured at 300 K.

by the MPM is excellent, but that fabricated by the CuO reduction was not sufficient for Hall effect measurement.

3. Kinetic study of Cu₂O thin film fabrication

In order to clarify the precise mechanism of Cu₂O formation from the Cu(II) complex, a kinetic study was performed using XRD [11]. In the study, it was clarified that the thermal reaction of the precursor film, which consists of a dibutylammonium salt of a [Cu(edta)]²⁻ complex ion, first produced metallic Cu species in Ar gas containing <10 ppm of air as an impurity. The Cu phase appeared gradually, and the amount of the phase could be determined from the area of the (111) peak of Cu. The activation energy (1.5 × 10² kJ mol⁻¹) of the reduction reaction from the Cu(II) complex to metallic Cu species was obtained by an Arrhenius plot over the temperature range 230–250°C. Above this temperature range, the Cu₂O phase was formed by the oxidation of the Cu phase under Ar gas flow. The amount of the Cu₂O phase could be determined from the area of the (111) peak. The activation energy (1.4 × 10² kJ mol⁻¹) of Cu₂O formation from the Cu phase was obtained by the Arrhenius plot over the temperature range 400–450°C. In order to examine the stability of the formed Cu₂O phase, the oxidation reaction rate from Cu₂O to the CuO phase in an identical atmosphere was also measured over the temperature range 450–475°C. The activation energy of the oxidation reaction from Cu₂O to the CuO phase was determined to be 1.0 × 10² kJ mol⁻¹. It was observed that the quality of the *p*-type Cu₂O thin film is strongly dependent on the mechanism of the low-temperature formation.

The XPS spectra of the films are shown in **Figure 5**. The peak positions of the Cu 2p_{3/2} level in spectra (a)–(d) are 933.5, 932.7, 932.5, and 933.2 eV in **Figure 5A**, respectively. The peaks observed in (a) and (d) can be assigned to the Cu²⁺ ion, and the broad peak at 944 eV observed in (d) is typical of CuO. In contrast, the peaks observed in (b) and (c) can be assigned to metallic Cu and/or Cu⁺ ions. These XPS results are consistent with the XRD results.

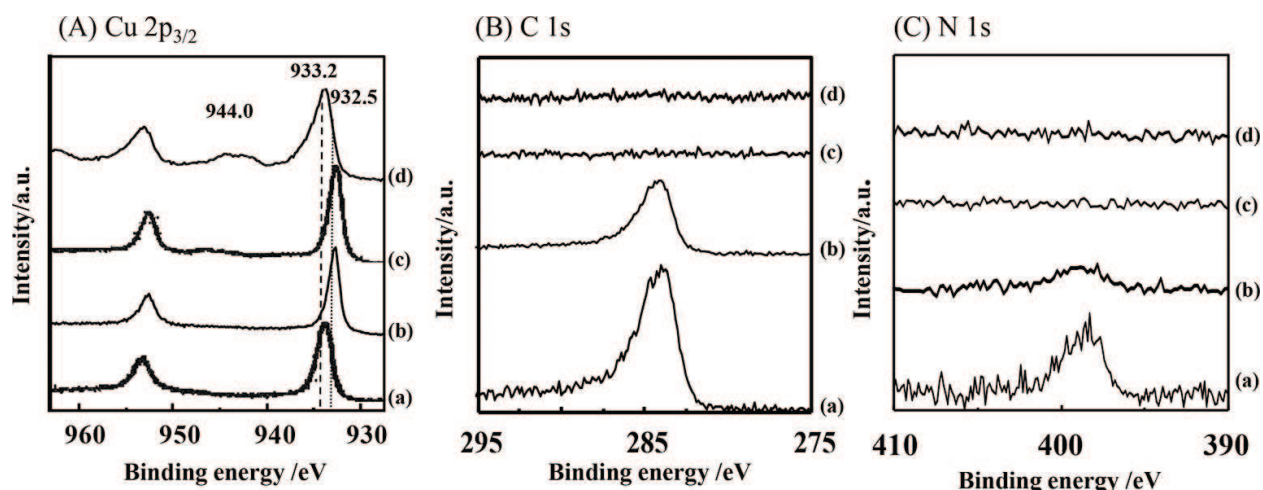


Figure 5. XPS spectra of (A) Cu $2p_{3/2}$, (B) C $1s$, and (C) N $1s$ of the thin films heat-treated in Ar gas flow. The films were fabricated by heat treating the precursor film at (a) 200°C for 10 min, (b) 400°C for 0 min, (c) 450°C for 10 min, and (d) 450°C for 60 min.

In **Figure 5B** and **C**, the XPS spectra of the C $1s$ and N $1s$ peaks, respectively, are shown. No impurities such as nitrogen or carbon atoms can be found in the XPS spectra of the resultant Cu_2O thin films, although the metallic Cu^0 thin film includes a certain amount of nitrogen and carbon atoms. It was thus clarified that single phase Cu_2O formation was completed by the removal of organic residues in the Cu^0 thin film. The co-presence of nitrogen and carbon atoms was thus shown to have an important role in preventing the oxidation of the produced Cu_2O phase. The presence of nitrogen and carbon atoms may also help in organizing the stepwise reactions.

In the sol-gel method for Cu_2O thin film formation, the CuO film is annealed at 900°C for 5 h in nitrogen for the partial removal of oxygen atoms from the initial oxide thin film. In contrast, the MPM eliminates the organic components in order to form the Cu_2O thin film at the abovementioned lower temperature. It is interesting that the difference between these two methods is in the kind of atoms that must be removed. Furthermore, it is important that the formation route of the p -type Cu_2O thin films determines the quality of the thin films, as mentioned above. The MPM is additionally preferable in terms of saving energy by reducing the formation temperature.

It was first shown that the expected Cu_2O formation using the MPM occurred via an unexpected intermediate Cu^0 phase formed by the thermal decomposition of the molecular precursor involving a Cu(II) complex salt. The XRD measurement of the crystallized thin films was useful in determining the activation energies of the redox reactions from the Cu(II) complex to Cu^0 , from Cu^0 to Cu_2O , and from Cu_2O to CuO (**Figure 6**). The redox reactions of the metals and organic ligands occurred stepwise with annealing of the thin films under moderate conditions. Consequently, the ligand in the molecular precursor plays an important role in fabricating excellent p -type Cu_2O thin films. It is also suggested that kinetic studies on the thermal reactions of metal complexes in the solid state are essential for revealing the reaction mechanism of thin film fabrication.

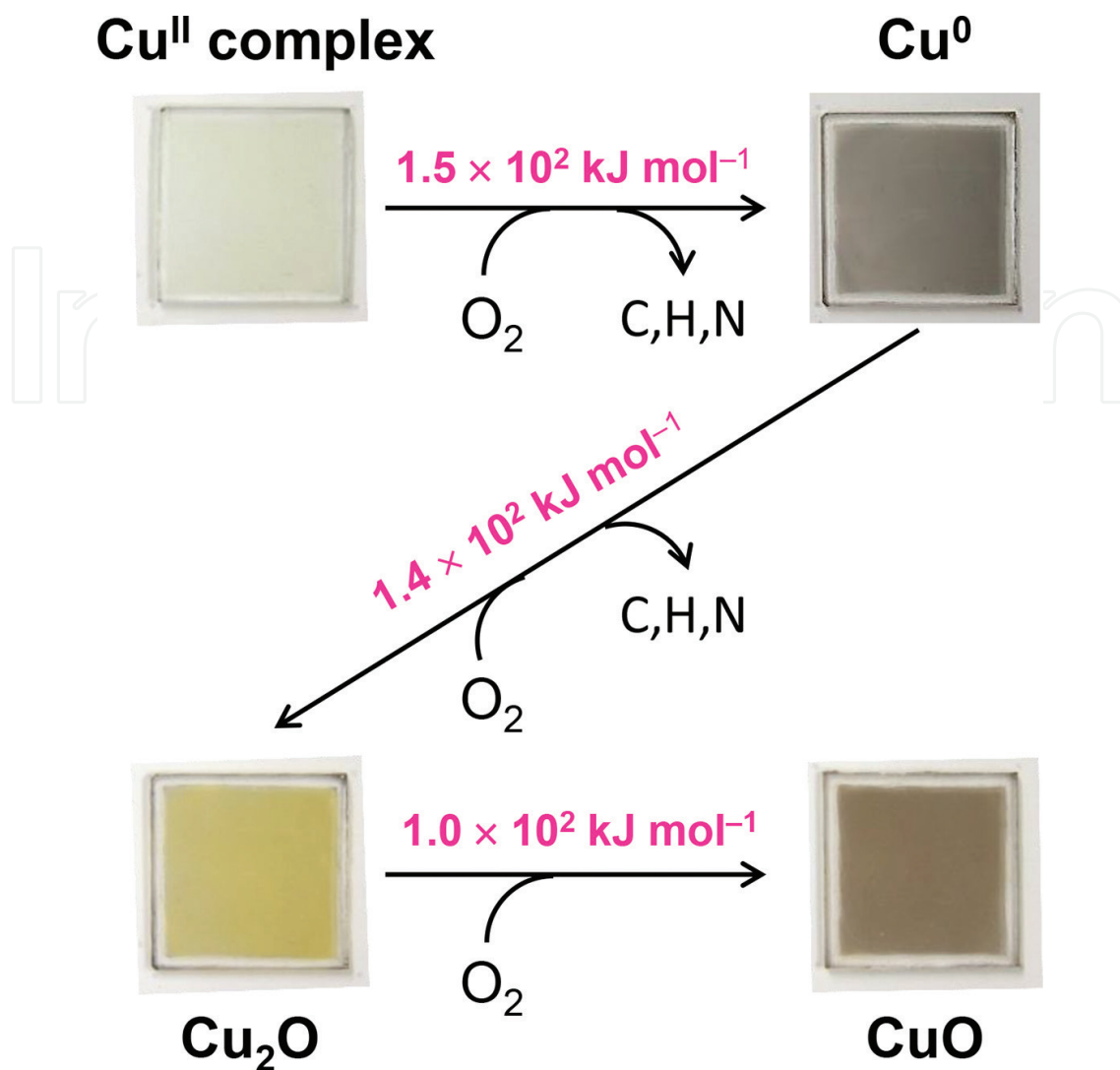


Figure 6. A kinetics study was performed in order to clarify the reaction mechanism for fabricating the excellent *p*-type Cu₂O thin films by using the molecular precursor method.

4. Fabrication of copper thin films

From the kinetic study of the Cu₂O thin film formation, it was elucidated that the Cu⁰ species formed as an intermediate was oxidized to the resultant Cu₂O thin film during the heat treatment, and the oxidizing agent is the oxygen present in the commercially available Ar gas as an impurity (<2 ppm) [11]. However, the intermediate Cu thin film obtained through the reaction using the precursor film is not electrically conductive. Therefore, in order to fabricate transparent metal copper thin films, we examined novel precursor solutions [35, 36]. A novel precursor solution containing a Cu²⁺ complex of EDTA and a Cu²⁺ complex of propylamine derived from formic acid, and the amine was prepared by mixing the two precursor solutions. The concentration of total copper in the ethanolic precursor solution was adjusted to 0.35 mmol g⁻¹. The spin-coating method was used for precursor film formation on a Na-free glass substrate. The spin-coated precursor films were preheated in a drying oven at 70°C for 10 min

and then, heat-treated at 350°C for 15 min under an Ar gas flow of 1.5 L min⁻¹ to fabricate thin films in a tubular furnace with a quartz glass tube. The resultant thin film is hereby denoted as **A**. The rate of temperature increase was controlled by a proportional-integral-derivative program preinstalled in the furnace. Before increasing the temperature, the tubular furnace was filled with Ar gas. The thickness of the resultant films was measured using a stylus profilometer. A flat- and same-sized quartz glass plate was placed on the resulting thin film **A** in the tubular furnace and then post-annealed at 350°C for 20 and 40 min in an Ar gas flow of 1.5 L min⁻¹. The resulting thin film is hereby denoted as **AP_n** (n = post-annealing time). The XRD patterns of the resultant thin films **A**, **AP₂₀**, and **AP₄₀** with a thickness of 40 nm over the 2θ range 30°–50° are shown in **Figure 7**. The peaks at 2θ = 36.6° and 42.5° for **A** can be assigned to the (111) and (200) phases of Cu₂O, respectively, and an additional peak at 43.5° for **A** is assigned to the (111) phase of copper (JCPDS card No. 04–0836). The peak at 2θ = 36.9° for **AP₂₀** is assigned to the (111) phase of Cu₂O and that at 43.7° can be assigned to the (111) phase of copper.

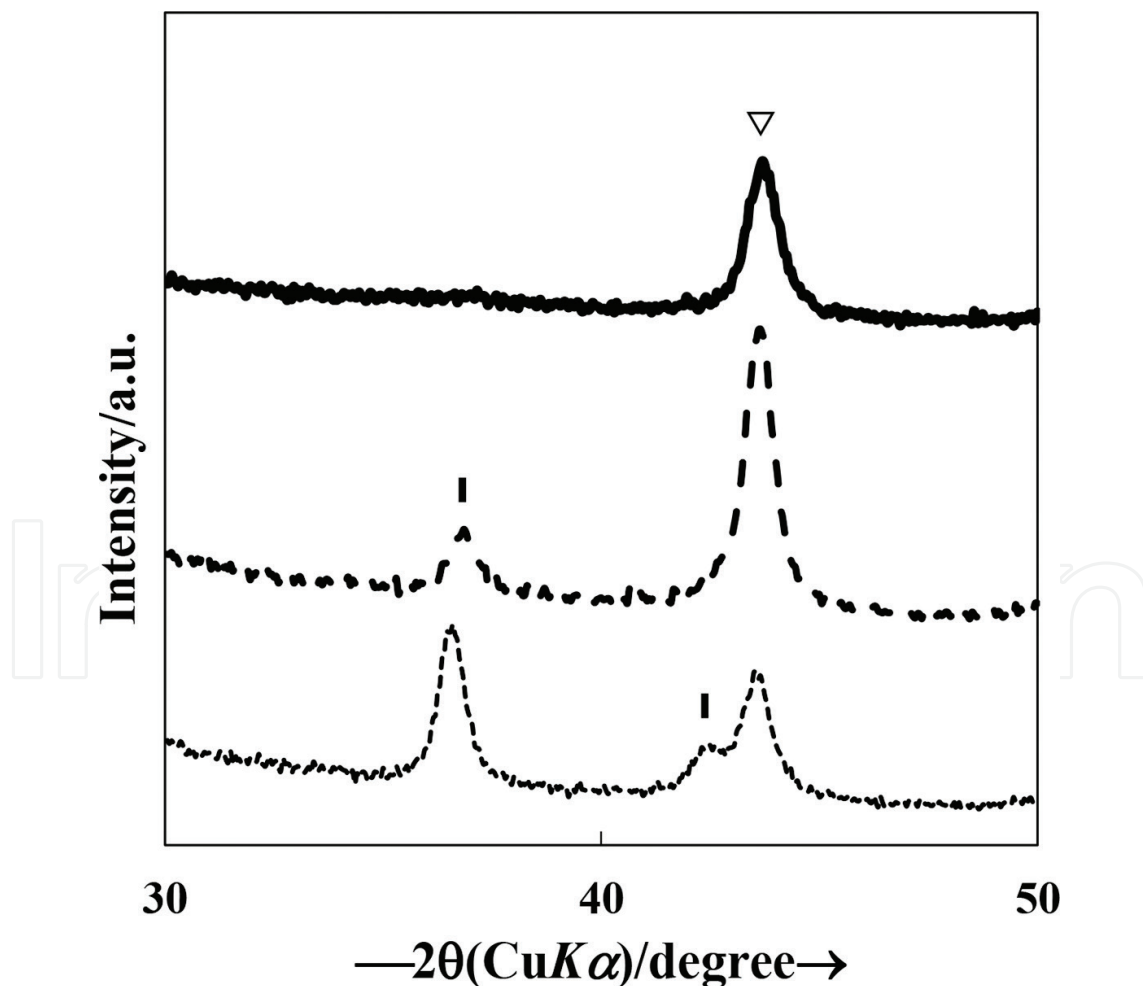


Figure 7. XRD patterns of **A**, **AP₂₀**, and **AP₄₀** thin films. Parallel beam optics ($\theta = 0.3^\circ$) was employed for calculations. The lines indicate the following:**A**, ----**AP₂₀**, and — **AP₄₀**. The peaks are denoted as follows: ▽ **Cu**; | **Cu₂O**.

The single peak at $2\theta = 43.7^\circ$ for **AP40** is attributed to the (111) phase of copper. Thus, the Cu₂O phase decreased gradually with increasing post-annealing time, and no peak owing to any impurity phase such as Cu₂O and CuO could be detected in the annealed **AP40** film. The cell parameter of the Cu cubic lattice in **A**, which was determined by the Wilson & Pike method, is $a = 3.71(3) \text{ \AA}$, and the crystallite size of Cu crystals formed in the film can be determined as 11(1) nm; the estimated standard deviations are presented in parentheses. The cell parameter of the Cu cubic lattice in **AP40** is $a = 3.72(3) \text{ \AA}$, and the crystallite size of the Cu crystals can be determined as 13(1) nm. The surface morphology of the **A** and **AP40** thin films was observed using FE-SEM. The grain size of the Cu particles also increased from 50 nm (**A**) to 70 nm (**AP40**) upon annealing. **Figure 8** shows the Auger spectra of **A**, **AP20**, and **AP40** thin films. Broad peaks were observed at 264 eV for carbon, 509 eV for oxygen, and 764, 835, and 914 eV for copper atoms. The kinetic energies of the copper atoms are identical to those in other films fabricated by the MPM. The result indicates that the amount of carbon atoms in the **AP40** thin film was reduced to half by the post-annealing treatment of **A**. **Figure 9** shows

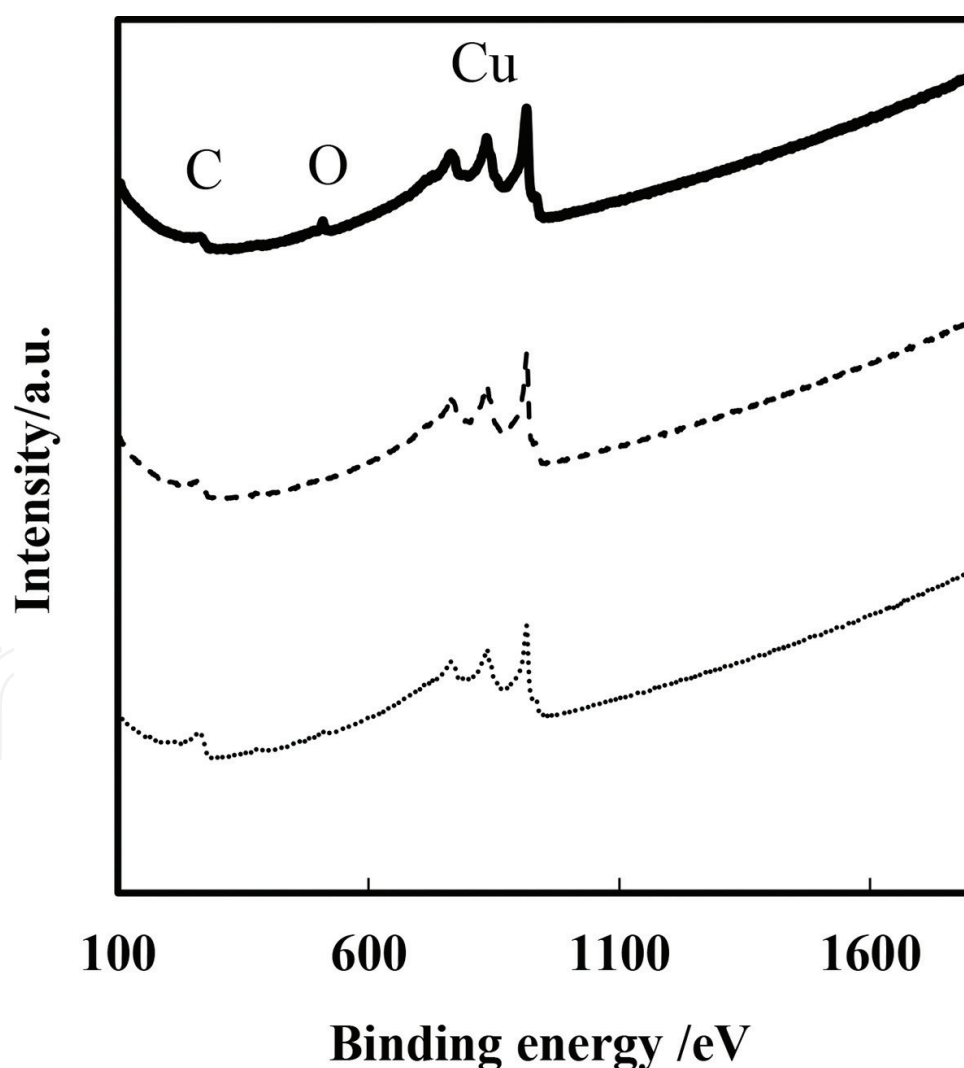


Figure 8. The Auger spectra of **A** and **A20**, and **AP40** thin films. The lines indicate the following:**A**, ----**AP20**, and —**AP40**, respectively.

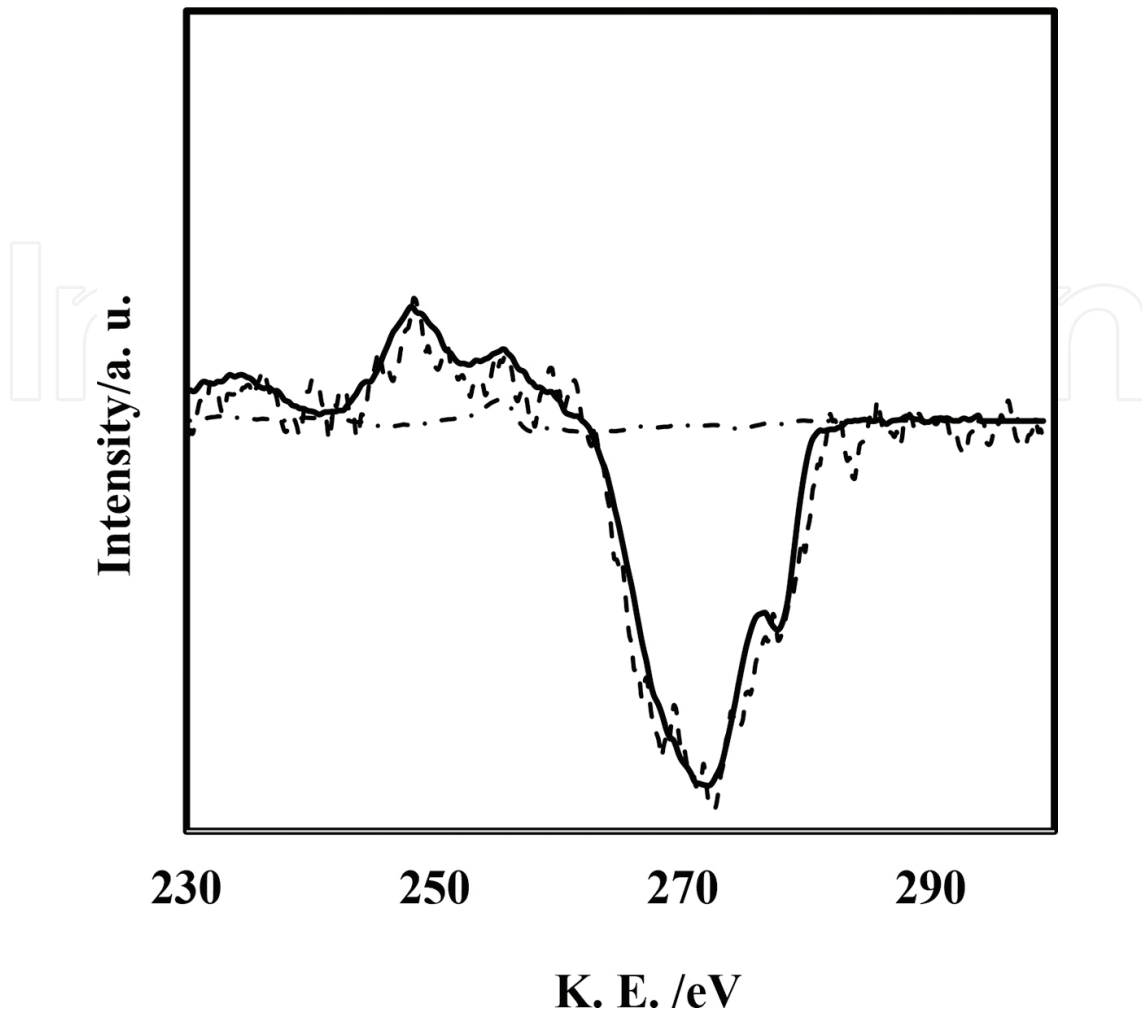
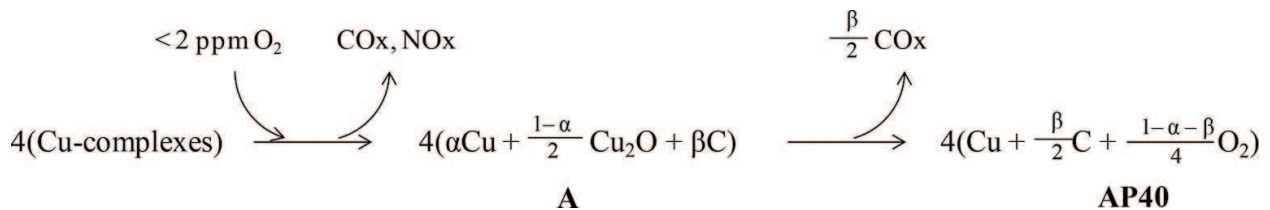


Figure 9. The curve fitting results of carbon state in AP40 thin film. The lines indicate the following:A, —Carbon (neutral), ----Carbon (tetravalent), respectively.

the curve fitting results of the Auger spectrum for **A** over the range 230–300 eV, corresponding to the carbon atoms, along with the curves of the neutral and tetravalent carbon atoms. The curve fitting results suggest that the carbon atom in **A** was 85% agreement to the neutral. The electrical resistivity of the **A**, **AP20**, and **AP40** thin films is 7.5×10^{-4} , 2.8×10^{-4} , and $4.7 \times 10^{-5} \Omega$ cm, respectively. Thus, highly conductive translucent copper thin films could be obtained in commercially available Ar gas. A plausible scheme for copper lattice formation, which can be deduced from the XRD and Auger spectra, is presented in **Scheme 1**.



Scheme 1. Plausible scheme for the formation of a Cu thin film from the precursor film.

The scheme indicates that four Cu complexes are required to construct one FCC copper unit cell. During the heat treatment of the precursor complexes in Ar gas flow containing <2 ppm of oxygen as impurity, neighboring complexes react with each other. The valency of copper was reduced from +2 to 0 by the thermal decomposition of the complexes of EDTA and butylamine ligands in Ar gas. In the process, Cu₂O involving Cu and the neutral carbon atom is produced in the **A** thin film. During the reaction from the **A** thin film to the resultant **AP40** thin film by post-annealing, when the oxygen content is below 2 ppm in the Ar gas, it cannot react with the film, because the quartz glass plate placed on the **A** thin film can prevent the film from encountering the oxygen molecule. In fact, the copper thin film, which was separately prepared by a vacuum plating method, was not oxidized by post-annealing under an identical condition. Thus, it is accepted that the reduction reaction occurred because of the materials inside the **A** thin film. Under these conditions, only one candidate that can act as a reductant for Cu²⁺ ion remains on the carbon atoms in film **A**.

The polycrystalline Cu lattices were gradually structured by reducing the valency of the Cu²⁺ ion with carbon atoms, and the Cu grains were simultaneously grown by annealing. This reaction mechanism involving the reduction reaction caused by carbon atoms may be comparable to the modern and indirect steel-making system using corks. The tensile strength of the **AP40** adhered onto the Na-free glass substrate was 36(12) MPa as determined from the stud pull adherence tests, indicating strong adhesion to the glass substrate. The tensile strength of the Cu film deposited onto an identical Na-free glass substrate by a vacuum plating method was 1.7(5) MPa after an identical heat treatment of the **AP40** thin film. Thus, the tensile strength of the **AP40** thin film on the Na-free substrate was more than 20 times higher than that of the Cu thin film deposited by the vacuum plating method. The covalent bonds between the trace amounts of Cu²⁺ ion present locally at the interface between the thin film **AP40** and the O²⁻ ions belonging to the Na-free glass molecules may assist in the formation of a robust interface between the Na-free glass substrate and the **AP40** thin film. In fact, the tensile strength of the adhesion of the Cu₂O thin film to the substrate fabricated using the MPM was 83(2) MPa.

Figure 10 presents the transmittance and reflectance spectra of the thin films. The transmittance spectra of **A**, **AP20**, and **AP40** are not significantly different in the UV-Vis region, and the transparency of **AP40** is more than ~30% in the visible region. The infrared reflectance of **AP40** is higher than 40% and reached 100% in the far-infrared region, whereas the reflectance of **A** was low, 20–30%, over this region. The MPM can facilely control the film thickness by adjusting the concentration of Cu ion in the precursor solution under identical spin-coating conditions. When the Cu thin film is 100-nm-thick, the conductivity is $1.8 \times 10^{-5} \Omega \text{ cm}$, and the transparency in the visible region is below 5%. Thus, a thicker film indicates higher conductivity, but reduced transparency.

Recently, we attempted to embed copper in narrow trenches (0.2–1.0 μm wide and 5.0 μm deep) by using the MPM. A new precursor solution was prepared by dispersing the Cu nanopowder (20–40 nm) into the abovementioned Cu precursor solution. Si substrates with the trenches were immersed in this precursor solution under ultrasonic vibration for 1 min and then slowly withdrawn from the solution. The dip coating and heat treatment steps were repeated twice. The cross-sectional FE-SEM images of the treated substrate indicate that the embedded copper fills the trenches without voids.

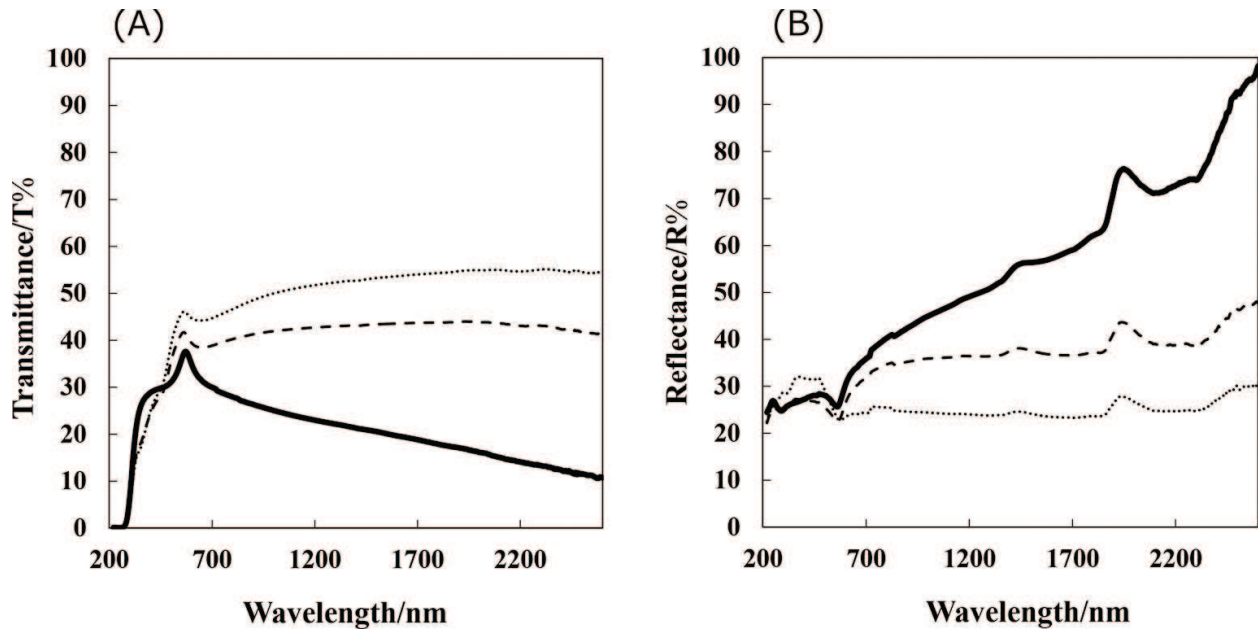


Figure 10. (A) The transmittance spectra of the resulting thin films. The lines indicate the following:A, ----AP20, and —AP40, respectively. (B) The reflectance spectra of the resulting thin films. The lines indicate the following:A, ----AP20, and —AP40, respectively.

5. Conclusion

Thermal reactions of metal complex films useful for ceramic thin film production such as Cu_2O did not attract much attention for a long time, with the exception of the CVD procedure. However, we indicated that the MPM provides facile and unique routes to obtain *p*-type Cu_2O and metallic Cu thin film with excellent adhesion to glass substrates, through the thermal reactions of metal complexes.

The importance of the metal complex in the MPM was presented by using the unprecedented thin film fabrication of *p*-type Cu_2O , along with the recently elucidated reaction mechanism. In general, impurities such as nitrogen and carbon atoms interfere seriously with the functions of semiconductor devices. However, the present molecular precursor involving nitrogen and carbon atoms is necessary for fabricating an excellent *p*-type Cu_2O thin film using this solution-based process. Additionally, in the chemical fabrication of copper thin films with high conductivity, an organic ligand that reacts with the central Cu(II) ion is essential, and the atoms derived from the ligand, which can act as a reductant, prevent the produced copper from oxidation.

It is important that most of the originally included atoms in the MPM system are not involved in the resultant thin films if the amounts and treatment are appropriate. Therefore, the role of the ligand of the metal complex resembles that of auxiliary lines to solve geometrical problems in mathematics. In the sol-gel process, the similarity of the gel composition and the final oxides is desirable and is supposed to be an advantage of the method, though the rearrangement of the polymerized amorphous species to the crystalline requires much energy. From this point of view, the concept of the MPM is quite different from that of the conventional sol-gel method and has many potential applications.

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