



# CO<sub>2</sub> Sensing Property of CuO-BaTiO<sub>3</sub> Mixed Oxide Film Prepared by Self-Assembled Multibilayer Film as a Precursor

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**Abstract.** Preparation of CuO-BaTiO<sub>3</sub> mixed oxide thin film by the decomposition of a self-assembled multibilayer film as a molecular template was investigated in this study. Furthermore, CO<sub>2</sub> sensing property of the resultant thin film was investigated as a capacitive type sensor. The self-assembled bilayer film of few 1000 layers thickness can be obtained easily by casting an aqueous suspension consisting of dimethyldihexadecylammonium bromide (DC1-16), Cu(ClO<sub>4</sub>)<sub>2</sub>, Ba(TiO(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>), 2,6-dimethyl-3,5-heptadione (DHP), and polyvinyl alcohol. Divalent copper ion (Cu<sup>2+</sup>) which is associated with 2 DHP molecules was incorporated into the molecular bilayer film and BaTiO<sub>3</sub> precursor exists at the interspace of molecular bilayer film by coordinating with polyvinyl alcohol. Upquenching the organic-inorganic film at 1173 K leads to the uniform film of CuO-BaTiO<sub>3</sub> oxide mixture. Although operating temperature shifted to higher temperature, the resultant film exhibits the capacitance change upon exposure to CO<sub>2</sub>. Consequently, it is concluded that the mixed oxide film of CuO-BaTiO<sub>3</sub> prepared by the decomposition of multibilayer film was also an appropriate capacitive type CO<sub>2</sub> sensor.

**Keywords:** CO<sub>2</sub> sensor, CuO-BaTiO<sub>3</sub> mixed oxide film, self-assembled multibilayer film

## 1. Introduction

Detection and/or control of CO<sub>2</sub> concentrations are strongly required in various industrial fields, e.g., smart air conditioner, food processing, and environmental monitoring. However, there is no commercialized sensor for detecting CO<sub>2</sub> except an infrared absorption method which proves to be expensive and rather difficult to miniaturize. Therefore, development of CO<sub>2</sub> sensor is strongly required and various types of sensors for detection of CO<sub>2</sub> have been proposed and extensively investigated [1–4]. At present, amongst proposed CO<sub>2</sub> sensors, solid electrolyte type sensors with an auxiliary phase such as Na<sub>2</sub>CO<sub>3</sub> or Li<sub>2</sub>CO<sub>3</sub> are the most popular [5]. However, it is pointed out that these type of sensors are strongly affected by humidity [6]. For the development of CO<sub>2</sub> sensor, therefore, it is required not only high sensitivity but also a superior selectivity. Although Miura et al. pointed out that incorporating

barium carbonate into the auxiliary phase is effective for reducing the influence of humidity [7], further improvement against humidity is required. Therefore, CO<sub>2</sub> sensor also requires a long term stability [8]. In the previous study, the authors have been investigated the mixed oxide of CuO-BaTiO<sub>3</sub> as a capacitive type CO<sub>2</sub> sensor [9]. An advantage of this capacitive type CO<sub>2</sub> sensor of CuO-BaTiO<sub>3</sub> is the negligible interference of humidity on CO<sub>2</sub> detection [10]. Furthermore, mixed oxide capacitor consisting of CuO, BaCO<sub>3</sub>, and CeO<sub>2</sub> are developed for the commercial CO<sub>2</sub> sensor by Matsushita Co. Ltd [11,12]. Therefore, capacitive type sensor has a great potential as the chemical sensor [12,13]. Our previous study also revealed that the electric energy barrier formed at a grain junction between CuO (p-type semiconductor) and BaTiO<sub>3</sub> (n-type semiconductor) had an important role for varying capacitance of the sensor element upon exposure to CO<sub>2</sub> [14]. Since the size of CuO is much larger than that of

BaTiO<sub>3</sub> [10], it is expected that the number of grain junction will increase with decreasing the particle size of CuO. Consequently, it is anticipated that CuO fine particle which is in contact with BaTiO<sub>3</sub> would be effective to improve the sensitivity and the response characteristics of the sensor.

On the one hand, preparation of inorganic film by decomposition of an ordered organic-inorganic composite film is highly attractive because the structure of the film can be controlled at an atomic level [15,16]. On this point of view, the authors investigated the preparation of CuO thin film on porous BaTiO<sub>3</sub> with the decomposition of the self-assembled multilayer organic film and it became clear that CuO film of fine particles can be prepared with the decomposition of the self-assembled multilayer film on porous BaTiO<sub>3</sub>. Also, the capacitance of the obtained CuO film on BaTiO<sub>3</sub> is highly sensitive to CO<sub>2</sub> [17]. On the other hand, inorganic cations are generally arranged in the hydrophilic layer of the interspace of bilayer or L-B films in the open literature reported until now. Therefore, organic-inorganic film in which different cations incorporated in different layer of the film have not been reported, however, in the biotic cell, not only interspace but also intraspaces of bilayer film are used. On this point of view, incorporation of the different cations into the different part of the organic-inorganic film is highly interesting. In the present study, authors newly designed the multilayer film of which Cu<sup>2+</sup> in hydrophobic (namely into molecular bilayer) and BaTiO<sub>3</sub> precursor in hydrophilic layer was investigated for the synthesis of BaTiO<sub>3</sub> and CuO mixed oxide at the atomic scale.

## 2. Experimental

Dimethyldihexadecylammonium bromide (143.8 mg, Sogo Pharmaceutical Co. denoted as DC1-16) of which molecular form is schematically shown in Fig. 1(a) was used as the template molecule of the multilayer film. 2,6-dimethyl-3,5-heptadione (7.8 mg, laboratory synthesis denoted as DHP) of which molecular form was also shown in Fig. 1(b), polyvinyl alcohol (17 mg) as binder and Cu(ClO<sub>4</sub>)<sub>2</sub> (9.3 mg) as a source of copper ion, and Ba(TiO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>) (5.6 mg) as BaTiO<sub>3</sub> precursor were dispersed in water (4 ml) by ultra sonic mixing for 3 min. After kept still for 15 min, the resultant clear blue solution was cast on a porous

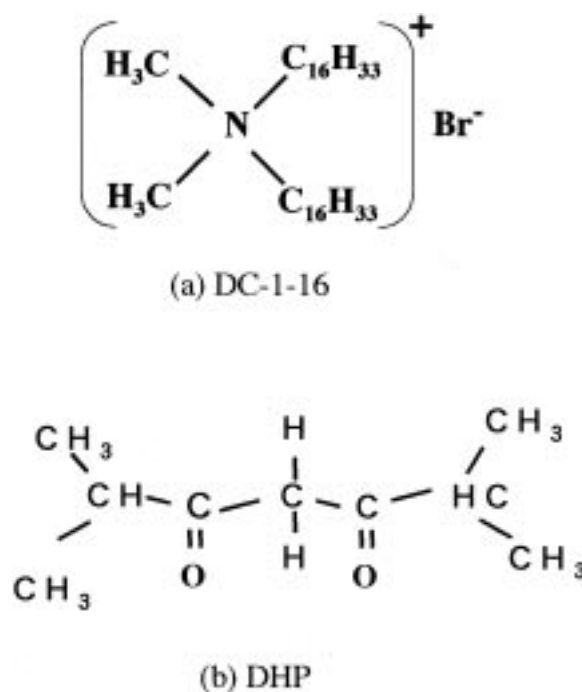


Fig. 1. Scheme of dialkylammoniumbromide (dc 1-16) (a) and 2,6-dimethyl-3,5-heptadione (DHP) (b) which are used for template molecules.

BaTiO<sub>3</sub> or SiO<sub>2</sub>-glass plate. Casting and drying at room temperature were repeated for 5 consecutive times at least before CO<sub>2</sub> sensing property was measured. A porous BaTiO<sub>3</sub> substrate (13 mm in diameter, 1 mm in thickness) was obtained by calcination at 1573 K for 4 h. The BaTiO<sub>3</sub> powder was prepared by calcination of an equimolar mixture of BaCO<sub>3</sub> and TiO<sub>2</sub> at 1473 K for 6 h. The cast film containing CuO and BaTiO<sub>3</sub> precursor on the porous BaTiO<sub>3</sub> substrate was decomposed thermally at 1173 K for 1 h to obtain mixed oxide film. The obtained film was analyzed by X-ray diffraction meter (Rigaku Rint-2000) with Cu K $\alpha$  line (40 kV, 50 mA). Nickel metal was used as a filter for removing K $\beta$  line. Ag paste (Tokuriki, 5 mm in diameter) was applied and dried at room temperature as the electrode on the obtained mixed oxide film.

CO<sub>2</sub> sensing characteristics were measured by ac two-probe method. Specimens were set in a ceramic tube which is connected to a gas flow system. The CO<sub>2</sub> concentration in sensing gas was controlled by diluting a commercial CO<sub>2</sub> with air. Air is always used as a reference gas in this study. The capacitance

of the element was measured with the LCR meter (HIOKI type 3502) at 50 kHz. Sensitivity of the element was expressed by a ratio of capacitance of CO<sub>2</sub> to that in air,  $C_{\text{CO}_2}/C_{\text{air}}$ .

UV-Visible spectra of Cu<sup>2+</sup>-DHP complex in hexane solution and in multibilayer film were measured with a transmission method and a diffuse reflection method, respectively, by the spectrometer (Hitachi, UV-350). ESR measurement was performed to determine the valence number and the regularity of Cu cations in the multibilayer film. Before measurement, sample was evacuated for 1 h and ESR measurement was performed at room temperature in vacuum by using Bruker EPR 380.

### 3. Results and Discussion

#### 3.1. Design of the Self-Assembled Multibilayer Film

Figure 2 shows the newly designed self-assembled multibilayer film in this study. Two molecules of DHP are coordinated with Cu<sup>2+</sup> to form a quadrangular planar compound and this compound is very stable and highly hydrophobic [17]. Therefore, it is expected that this Cu-DHP compound will be existed in the hydrophobic part of multibilayer film, namely intraspaces of the molecular bilayer film as shown in Fig. 2. In addition, BaTiO<sub>4</sub> cation as a BaTiO<sub>3</sub> precursor, which is hydrophilic, is coordinated with polyvinyl alcohol and it will be existed in the hydrophilic part of the multibilayer film, namely interspaces of molecular bilayer film. Therefore, in this newly designed multibilayer film, CuO and BaTiO<sub>3</sub> precursor cations are accommodated alternatively within the molecular bilayer film consisting of dc 1–16 at an atomic scale. After removing the organic compound and oxidizing the inorganic cations, it is expected that oxide film of CuO and BaTiO<sub>3</sub> mixing at the atomic level can be obtained.

#### 3.2. Preparation of Molecular Template of Multibilayer Film for CuO Thin Film

Figure 3 shows the X-ray diffraction pattern of the resultant cast film on the glass substrate. It is obvious that the organic film exhibits the diffraction pattern which is the typical layered structure. Therefore, the results of XRD measurement suggest that the resultant

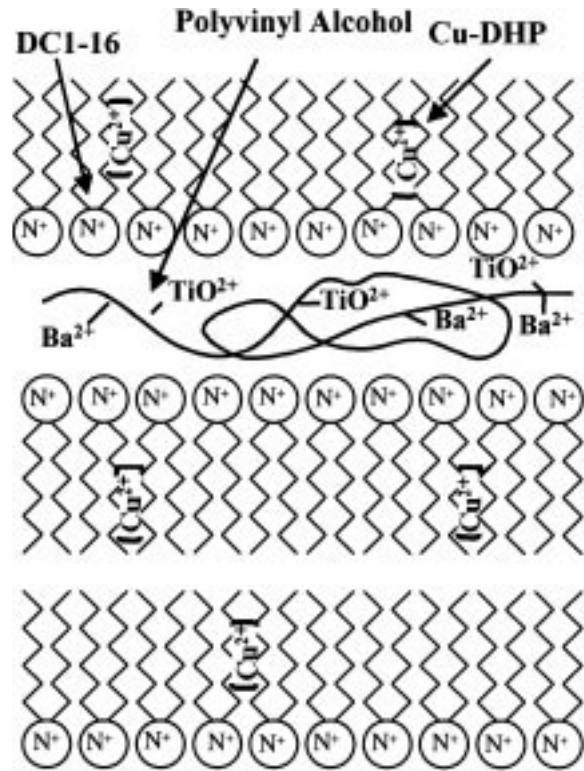


Fig. 2. Scheme of the designed self-assembled multibilayer film.

cast film has a long-range regularity and this structure is layered ones. Thickness of the bilayer film is estimated by using Bragg's Law with  $n = 2$  for the

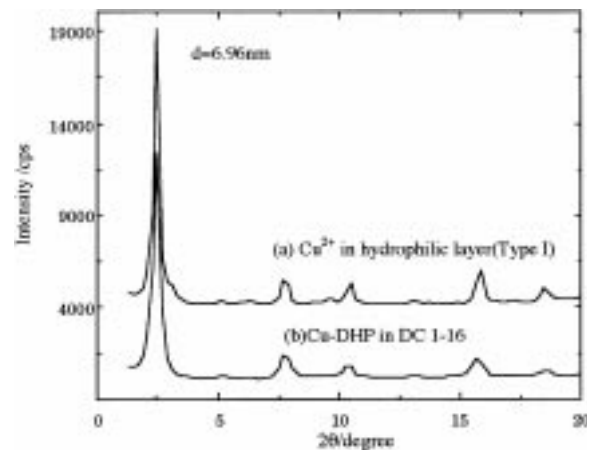


Fig. 3. X-ray diffraction pattern of obtained casting film on glass substrate. (a) Cu<sup>2+</sup> located at the hydrophilic layer with dimethyl amine in dc 1–16 film, (b) Cu<sup>2+</sup> located at the hydrophobic layer with DHP in dc 1–16 film.

diffraction peak at the lowest diffraction angle. By averaging  $d$  values estimated from the each peaks, the intraplanar distance of the final film is found as 6.96 nm. This intraplanar distance should correspond to the thickness of the each bilayer film consisting of dc 1–16. In Fig. 3, XRD pattern of the cast film in which  $\text{Cu}^{2+}$  was incorporated into the hydrophilic layer by using a modified ethylenediamine in the previous study (denoted as Type I) was also shown in Fig. 3(a) for comparison. Comparing the XRD pattern of Type I multibilayer film, no significant difference was observed not only on the diffraction angle but also on the relative strength of X-ray diffraction peaks. This suggests that the introduction of Cu-DHP complex did not affect the arrangement of molecular bilayer film. Considering the planer structure of Cu-DHP complex, it is considered that Cu-DHP molecule will parallel along the alkyl chain of dc 1–16 provided that Cu-DHP complex will be incorporated into molecular bilayer film.

To confirm the part of  $\text{Cu}^{2+}$  cations in self assembled multibilayer film, ESR and UV-Visible spectra were measured. Cu-DHP complex exhibits the broad but the characteristic absorption band around 650 nm in UV-Visible absorption spectra [18]. Figure 4 shows the UV-Visible spectra of Cu-DHP complex in the hexane solvent and that in self assembled multibilayer film prepared. It is clear that similar UV-Visible absorption band which assigned to Cu-DHP

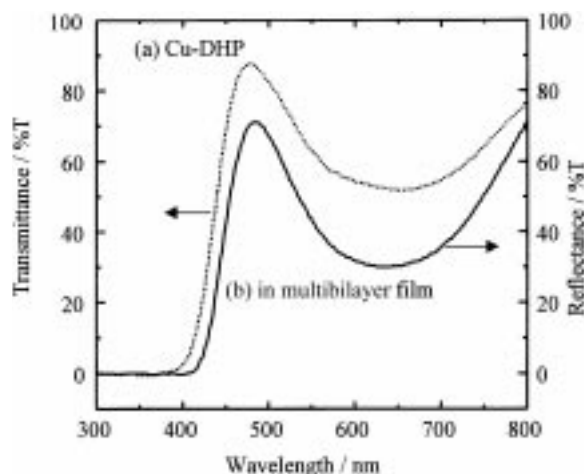


Fig. 4. UV-Visible spectra of Cu-DHP complex in hexane (a) and the obtained casting film (b).

complex was observed in the obtained self-assembled multibilayer film. This suggest that Cu-DHP complex was stably contained in the self-assembled multibilayer film. Since it is well-known that Cu-DHP complex is highly hydrophobic, it seems most likely that  $\text{Cu}^{2+}$  seem to be introduced into the molecular bilayer.

Figure 5 shows the ESR spectra of the obtained self-multibilayer film as a function of incident angle of magnetic field. It was shown that ESR signal of  $\text{Cu}^{2+}$  was monotonously decreased with increasing the incident angle of magnetic field when  $\text{Cu}^{2+}$  was arranged in the hydrophilic layer by using modified ethylenediamine [17,19,20]. Therefore, ESR measurement is effective to get information on the circumstance of  $\text{Cu}^{2+}$  ion in the multibilayer film. No regularity can be expected on  $\text{Cu}^{2+}$  in the designed organic-inorganic film in the present study. Consequently, if Cu-DHP complex will exist into the bilayer film, it is expected that the angular dependence of ESR signal will be disappeared. Clearly, the single peak which is assigned to  $\text{Cu}^{2+}$  is observed on the ESR spectra of cast film. Therefore, the valence number of Cu ion in the self-assembled multibilayer film is divalent. In similar with the results of previous study, the hyperfine structure which suggests the highly dispersing state was not observed on ESR signal of  $\text{Cu}^{2+}$  as shown in Fig. 5. On the other hand, in good agreement with the expectation,

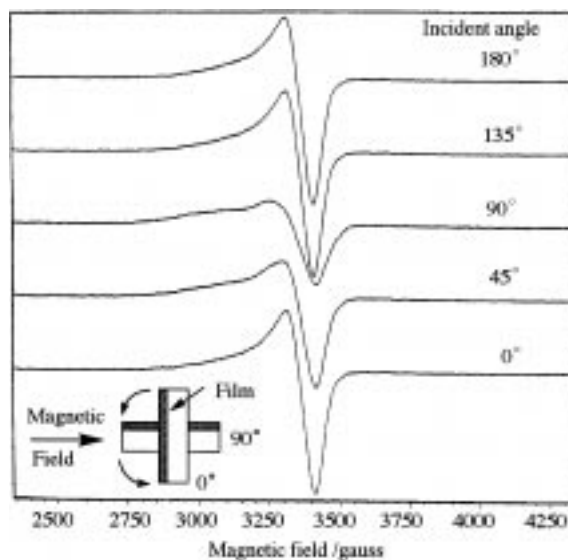


Fig. 5. ESR spectra of Cu in casting film as a function of incident angle of magnetic field.

the strength of Cu<sup>2+</sup> ESR peak was almost independent of the incidence angle of magnetic field. This result suggests that Cu<sup>2+</sup> cation has no regularity in the self-assembled multibilayer film. Considering all results discussed and hydrophobic property of Cu-DHP, it is quite reasonable that Cu-DHP exists at the intraspaces of molecular bilayer film and parallels along the alkyl chains of dc 1–16.

Since it seems most likely that Cu<sup>2+</sup> cations successfully introduce into the molecular bilayer film, introduction of BaTiO<sub>3</sub> precursor cations into the hydrophilic layer of casting film was investigated. Since the number of titanias acid soluble into water is limited and dc 1–16 is easily decomposed in acidic solution, the authors adopted Ba(TiO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>) as a precursor of BaTiO<sub>3</sub>. Figure 6 shows the XRD pattern of the self-assembled multibilayer film in which Cu<sup>2+</sup> introduced into molecular bilayer film and BaTiO<sub>3</sub> precursor between the molecular bilayer film. Since polyvinyl alcohol has a high capability to associate with the metal cations, it is expected that BaTiO<sub>3</sub> precursor ion is coordinated with polyvinyl alcohol and exist at the hydrophilic layer of the multi-assembled bilayer film, namely, an interspace of molecular bilayer film. It is clear that the similar XRD pattern with that in Fig. 3 was exhibited on the self-assembled film in which BaTiO<sub>3</sub> precursor cation was introduced. Here, it is also noted that the interplanar distance of the bilayer film was also independent of the introduction of BaTiO<sub>3</sub> precursor cations. Therefore, it is considered that the self-assembled

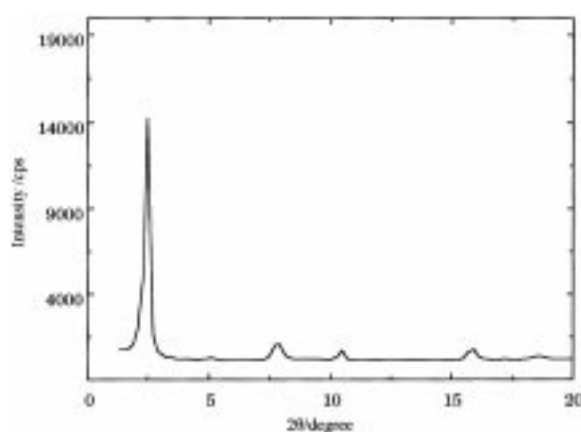


Fig. 6. XRD pattern of the obtained dc 1–16 self-assembled multibilayer film containing Cu<sup>2+</sup>-DHP complex molecule and BaTiO<sub>3</sub> precursor cation.

multibilayer film which contains Cu<sup>2+</sup> and BaTiO<sub>3</sub> precursor cations in hydrophobic and hydrophilic layer respectively was obtained. It was also confirmed by ICP analysis that the amount of Ba, Ti, and Cu contained in the self-assembled multibilayer film was identical to the targeted equimolar amount of CuO and BaTiO<sub>3</sub>. Therefore, it is expected that CuO-BaTiO<sub>3</sub> mixture at the highly dispersing state will be obtained by the thermal decomposition of the obtained cast film.

### 3.2. Removal of the Organic Template by Calcination

To obtain an oxide film, the regularly arranged organic film should be removed and the inorganic cation should be oxidized without destroying the regularity in the precursor film. This is simply performed by a heat treatment in air. The calcination condition of the cast film to obtain the CuO film was also investigated in the previous study and it became clear that the organic film of dc 1–16 can be removed by the calcination at temperature higher than 673 K [17]. In addition, upquenching to the decomposition temperature (ca. 1173 K) is better than heating at constant rate to obtain the inorganic film without destroying the regularity. Therefore, in this study, upquenching of the self-assembled multibilayer film containing Cu<sup>2+</sup>, Ba<sup>2+</sup> and TiO<sup>2+</sup> cations was performed to obtain the mixed oxide capacitor film of CuO and BaTiO<sub>3</sub>. It is also noted that preparation of mixed oxide film, in particular, two phase mixture by using the organic-inorganic film has been limited in number of open literature. Figure 7 shows the XRD pattern of the obtained oxide film by the calcination of the self-assembled multibilayer film on the quartz substrate at 1173 K for 1 h. It is clear that XRD pattern of the obtained film was consisted of the diffraction peaks from BaTiO<sub>3</sub> and CuO, although the weak peaks from an unknown phase were also observed. At present, this unknown phase is anticipated to be assigned to the compound containing Ba and Ti. This is because there are a lot of phases exist in barium-titanium oxide. It is also noted that the BaTiO<sub>3</sub> film with the single perovskite phase was obtained by the calcination of multibilayer film containing Ba<sup>2+</sup> and TiO<sup>2+</sup> cations at 1173 K for 1 h. Therefore, it seems likely that the formation of BaTiO<sub>3</sub> was also affected by the coexistence of Cu<sup>2+</sup>. Any way, it became clear that the oxide film consisting of BaTiO<sub>3</sub> and CuO was

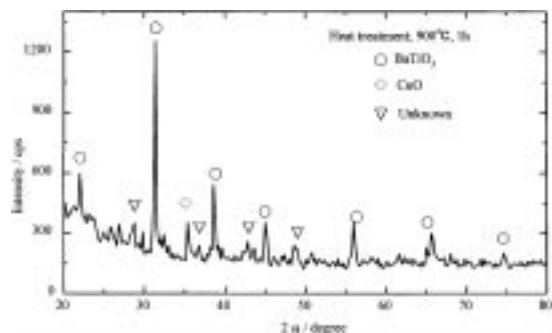


Fig. 7. XRD pattern of the obtained casting film after upquenching at 1173 K.

successfully prepared by the decomposition of the self-assembled multilayer film.

Figure 8 shows the SEM observation results of the obtained CuO-BaTiO<sub>3</sub> film. Although the crack and the hole were observed in places, uniform oxide film consisting of fine particles was generally obtained by the decomposition of the self-assembled multilayer film as shown in Fig. 8(a). On the other hand, there are lot of particles observed on film as shown in Fig. 8(a). This may suggest that during calcination, some part of the self-assembled film was peeled and decomposed. However, the resulting particle as well as film were dense in spite of the low calcination temperature of 1173 K as shown in Fig. 8(b). Therefore, the fine particle of CuO and BaTiO<sub>3</sub> seem to be formed at the initial stage and consequently, sintering occurred faster to increase the density even at low temperature. It is well-known that the porosity is an important factor for the gas sensor, in particular, the ceramic gas

sensor. Therefore, one should pay attention on the calcination condition of the multilayer film for obtaining the oxide film for sensor element. It is also confirmed that CuO and BaTiO<sub>3</sub> were distributed uniformly in the particle and no significant aggregation was observed by the EDX analysis at high magnification. Therefore, it can be said that CuO and BaTiO<sub>3</sub> oxide film in which both oxides were mixed property was obtained by the decomposition of the self-assembled multilayer film.

### 3.3. CO<sub>2</sub> Sensing Characteristics of the CuO-BaTiO<sub>3</sub> Mixed Oxide Prepared by the Decomposition of Self-Assembled Multilayer Film

Figure 9 shows the effects of the decomposition temperature of self-assembled film on the sensitivity to 2% CO<sub>2</sub> of CuO-BaTiO<sub>3</sub> mixed oxide film on porous BaTiO<sub>3</sub> substrate. No change in capacitance was exhibited on the BaTiO<sub>3</sub> substrate itself upon exposure to CO<sub>2</sub>, however, the change in capacitance was observed after deposition of CuO-BaTiO<sub>3</sub> mixed oxide film on it. Sensitivity to 2% CO<sub>2</sub> was strongly dependent on the calcination temperature of the multilayer film and the maximum sensitivity to 2% CO<sub>2</sub> was obtained on the film which was calcined at 1173 K. Since the porosity of film decreased with increasing calcination temperature, the excessively high calcination temperature only decrease the sensitivity to CO<sub>2</sub>. On the other hand, the decomposition of multilayer film or removing the carbonous compound seems to be insufficient when calcination temperature is low. Therefore, it is

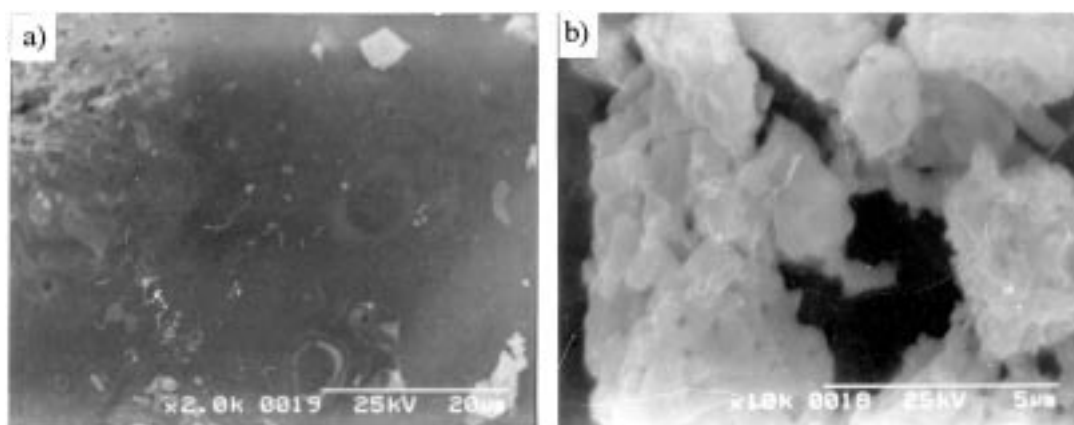


Fig. 8. SEM observation results of the obtained film (a) and the high magnification observation of particle on film (b).

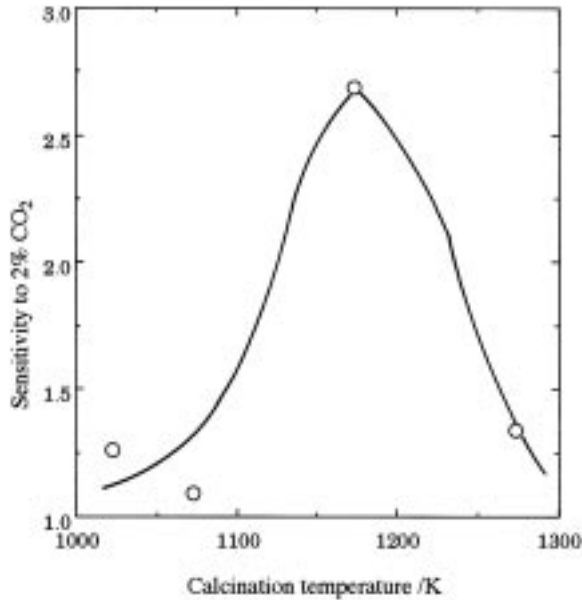


Fig. 9. Sensitivity to 2% CO<sub>2</sub> on BuO-BaTiO<sub>3</sub> film at 948 K as a function of the calcination temperature.

considered that the optimized decomposition temperature for self-assembled multilayer film exist around 1173 K.

Figure 10 shows the temperature dependence of the sensitivity to 2% CO<sub>2</sub> of CuO-BaTiO<sub>3</sub> mixed oxide film on the BaTiO<sub>3</sub> porous substrate. Temperature dependence of the sensitivity of CuO-BaTiO<sub>3</sub> oxide mixture was also shown in Fig. 10 for comparison. It is obvious that CuO-BaTiO<sub>3</sub> mixed oxide film prepared in this study exhibits the capacitance change at higher temperatures (from 873 to 973 K) comparing with CuO-BaTiO<sub>3</sub> powder mixture. Considering the SEM observation results in Fig. 8, the shift in the operating temperature to higher temperature may be attributed to the low porosity in the film. In addition, the maximum sensitivity to 2% CO<sub>2</sub> is 2.7, which is almost the same as that of CuO-BaTiO<sub>3</sub> powder mixture. In case of the CuO film on BaTiO<sub>3</sub> substrate, the sensitivity to CO<sub>2</sub> becomes twice, although the highest sensitivity was attained at the high operating temperature of 973 K [17]. Therefore, there is a possibility that the sensitivity is increased by controlling the porosity of film, namely, further optimizing the decomposition condition. The impurity phase detected by XRD measurement is also considered as another reason for low sensitivity comparing that of the CuO film deposited on BaTiO<sub>3</sub> substrate. Although the high sensitivity was

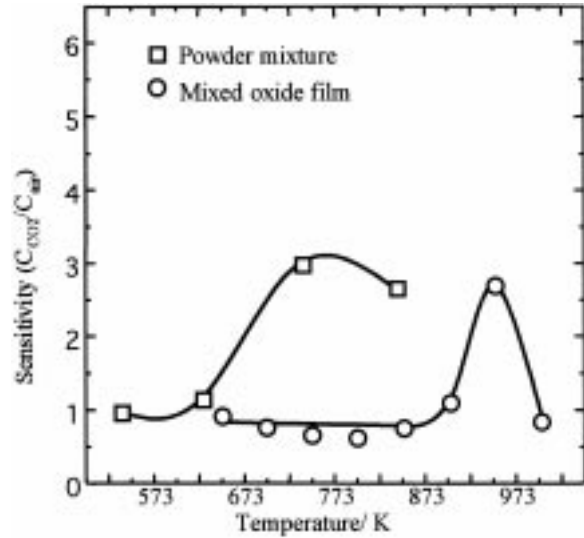


Fig. 10. Temperature dependence of the sensitivity of CuO-BaTiO<sub>3</sub> film and bulk element to 2% CO<sub>2</sub>. Measurement frequency is 50 kHz.

obtained at 950 K, the capacitance of the film was gradually shifted to a lower value in air. Therefore, it is expected that the high operating temperature is not desired from the long term stability point of view. The suitable operating temperature of this CuO-BaTiO<sub>3</sub> film seems to exist at slightly lower temperature around 900 K.

The capacitance of CuO-BaTiO<sub>3</sub> mixed oxide film shows a good reproducibility to the response on exposure to CO<sub>2</sub> at 948 K. Figure 11 shows the response characteristics of CuO-BaTiO<sub>3</sub> mixed oxide film to 2% CO<sub>2</sub> at 948 K. The period for 80% in response and recovery was 48 and 150 s, respectively. On the other hand, the oxide mixture of CuO and BaTiO<sub>3</sub> exhibited rapid response to CO<sub>2</sub> and the 80% response was attained within 25 s [13]. However, it takes a long period to recover to the original level (80% recovery period is 180 s). Therefore, the response time became longer on the CuO-BaTiO<sub>3</sub> mixed oxide film in spite of the elevated operating temperature. The prolonged response time was also assigned to the insufficient porosity of film. On the other hand, the insufficient porosity of film was also delayed the removal of CO<sub>2</sub> from element resulting in the longer recovery time of film considering the high operating temperature. Any way, this study made clear that the mixed oxide film of CuO-BaTiO<sub>3</sub> of which capacitance was dependent on CO<sub>2</sub>

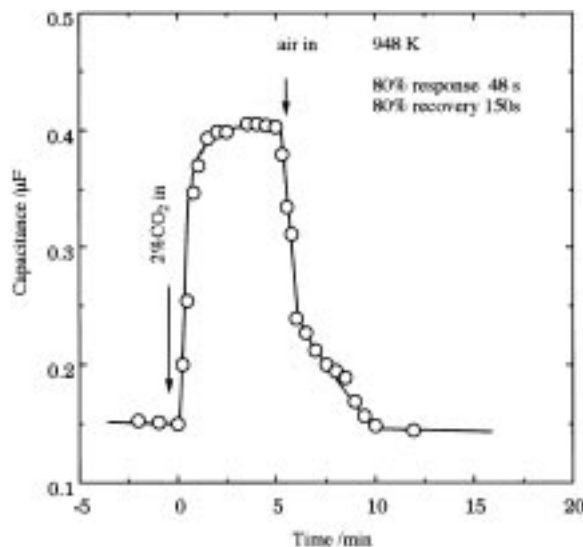


Fig. 11. Response curve to 2% CO<sub>2</sub> on CuO-BaTiO<sub>3</sub> at 948 K.

concentration can be prepared by the decomposition of the self-assembled multibilayer film as a molecular template. Further detail study on the decomposition of multibilayer film to obtain the moderate porosity are now under investigation.

#### 4. Conclusion

Preparation of CuO and BaTiO<sub>3</sub> mixed oxide thin film by the self-assembled multibilayer organic film was investigated for the capacitive type CO<sub>2</sub> sensor. The multibilayer film in which Cu<sup>2+</sup> and BaTiO<sub>3</sub> precursor cations exist at intraspaces and interspaces of bilayer film can be successfully prepared by using DHP and polyvinyl alcohol for the ligand of Cu<sup>2+</sup> and BaTiO<sub>3</sub> precursor cations respectively. Uniform but slightly dense CuO-BaTiO<sub>3</sub> mixed oxide film was obtained by the removal of the self-assembled multibilayer film by a heat treatment at 1173 K. Since sintering of the formed powder was easily proceeded resulting in the insufficient porosity, the obtained CuO-BaTiO<sub>3</sub> mixed oxide film exhibited the capacitance change at temperature higher than 873 K

and longer response and recovery period. However, CuO-BaTiO<sub>3</sub> mixed oxide film responding to CO<sub>2</sub> can be prepared through the self-assembled multibilayer film. In this point of view, preparation of an inorganic film by oxidizing cations arranged with atomic level regularity is an attractive method for the preparation of the useful materials for gas sensors.

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