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Preparation of CuO thin films on porous $BaTiO_3$ by self-assembled multibilayer film formation and application as a CO_2 sensor

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Preparation of CuO thin films by decomposition of self-assembled multibilayer films as a molecular template was investigated. Furthermore, the CO_2 sensing property of the resultant CuO thin films on a porous $BaTiO_3$ was investigated as a capacitive type sensor. Self-assembled bilayer films of a few 1000 layers thickness can be readily obtained by casting an aqueous suspension composed of dimethyldihexadecylammoniun bromide (DC1–16), $Cu(CH_3CO_2)_2$, hexadecylethylenediamine and poly(vinyl alcohol). Divalent copper ions (Cu^{2+}) which are associated with two hexadecylethylenediamine molecules were arranged in the hydrophobic layer of the multibilayer film. Rapid heating to the combustion temperature of DC1–16 was desirable for removing organic molecules in the multibilayer template. Thin films of CuO can be obtained by calcination at temperatures higher than 573 K. The resultant CuO thin films were porous and consisted of fine particles. The capacitance of CuO thin films prepared from self-assembled multibilayer films as a molecular template on the $BaTiO_3$ porous substrate exhibited a high sensitivity to CO_2, which is twice that of a conventional mixed oxide capacitor of CuO–$BaTiO_3$. The capacitance of CuO thin films on $BaTiO_3$ increases with increasing CO_2 concentration in the range from 100 ppm to 50% at 873 K. Consequently, it is concluded that CuO thin films on $BaTiO_3$ were appropriate capacitive type CO_2 sensors.

1 Introduction

Detection and control of CO_2 concentrations are of substantial importance in various industrial fields, *e.g.* smart air conditioning, food processing, and environmental monitoring. However, there is no effective method to detect CO_2 except IR absorption which is expensive and is difficult to miniaturize. Therefore, various types of sensors for detection of CO_2 have been proposed and extensively investigated.[1–4] At present, amongst proposed CO_2 sensors, solid electrolyte type sensors with an auxiliary phase such as $LiCO_3$ are the most popular. However, it is pointed out that these types of sensors are strongly affected by humidity.[5] For the development of CO_2 sensors, therefore, not only a high sensitivity but also a superior selectivity is required. Miura *et al.* pointed out that incorporating barium carbonate into the auxiliary phase is effective in reducing the influence of humidity.[6] Furthermore, CO_2 sensors also require a long term stability and solid electrolyte type CO_2 sensors are extensively investigated to improve their long term stability which is adversely influenced by change in electrode activity.[7] In a previous study, we investigated the mixed oxide CuO–$BaTiO_3$ as a capacitive type CO_2 sensor.[8] An advantage of this capacitive type CuO–$BaTiO_3$ CO_2 sensor is the negligible interference by humidity on CO_2 detection.[9] Therefore, CuO–$BaTiO_3$ may be utilized as a CO_2 sensor which can be practically used for monitoring CO_2 concentration.[10] In the present study, CO_2 sensing characteristics of CuO thin films on $BaTiO_3$ were investigated as a capacitive type sensor. Our previous study revealed that the electric energy barrier formed at a grain junction between CuO (p-type semiconductor) and $BaTiO_3$ (n-type semiconductor) had an important role in varying the capacitance of the sensor element upon exposure to CO_2.[11] Consequently, it is expected that CuO fine particles in contact with $BaTiO_3$ would be effective to improve the sensitivity and the response characteristics of the sensor.

On the other hand, a thin film of oxide which can detect gases is an attractive subject, because miniaturization of the sensor element is feasible with a possibility to improve the sensitivity or response characteristics. In particular, an increase in sensitivity is expected for a capacitive type sensor, because the signal level is increased by decreasing the thickness. A number of physical and chemical methods have been proposed for the preparation of thin films. Among these, preparation of inorganic films by decomposition of an ordered organic–inorganic composite film, denoted the molecular template method, is highly attractive because the structure of the film can be controlled at an atomic level. The molecular template method leads to an inorganic thin film by oxidizing the inorganic cation which is regularly arranged in a layered organic molecule as template. For organic templates, many compounds have been investigated and, amongst them, Langmuir–Blodgett (LB) films are the most extensively studied.[12] However, as far as the preparation of inorganic film is concerned, the amount of cation incorporated into a single LB film is insufficient to obtain a continuous inorganic film. Therefore, accumulation of LB film to a few 1000 layers is essential for the preparation of inorganic films. The lamination of films requires extended times and sometimes regularity in film is compromised during accumulation. In contrast, the casting method as proposed by Kimizuka and Kunitake[13] is a better method to obtain accumulated bilayer template films consisting of a few 1000 layers. In this method, an aqueous micelle consisting of an organic molecule which contains both hydrophilic and hydrophobic groups and inorganic cations is spread on a substrate and the bilayer film of a few 1000 layers is self assembled during drying of the cast suspension. While not suitable for preparing single layered organic films this method is suitable for preparing multibilayer organic films which have adequate thickness to support a uniform inorganic film. In the present study, we investigate the preparation of

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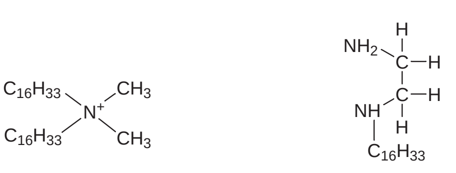
CuO thin films on porous $BaTiO_3$ substrate using the modified Kimizuka casting method.

2 Experimental

Dimethyldihexadecylammonium bromide [DC1–16 Sogo Pharmaceutical Co., Fig. 1(*a*)] was used as the template molecule to form bilayer films. Dimethyldidodecylammonium bromide (0.1438 g), hexadecylethylenediamine [14.2 mg, Fig. 1 (*b*)], polyvinyl alcohol (17 mg) as binder and $Cu(O_2CCH_3)$ (4.9 mg) as a source of copper ion were dispersed in water (5 ml) by ultrasonication for 3 min. After keeping undisturbed for 15 min, the resultant clear blue solution was cast on a porous $BaTiO_3$ or SiO_2 glass plate. Casting and drying at room temperature were repeated five times before CO_2 sensing properties were measured. A porous $BaTiO_3$ substrate (13 mm diameter, 1 mm thickness) was obtained by calcination at 1573 K for 4 h. The $BaTiO_3$ powder was prepared by calcination of an equimolar mixture of $BaCO_3$ and TiO_2 at 1473 K for 6 h. The cast film containing Cu cations on the porous $BaTiO_3$ substrate was decomposed thermally at 1173 K for 30 min to obtain the CuO film. The obtained films were analyzed by X-ray diffraction (Rigaku Rint-2000) with Cu-Kα radiation (40 kV, 50 mA). Nickel was used to filter out Ni-Kβ radiation. Ag paste electrodes (Tokuriki, 5 mm diameter) were applied and dried at room temperature on the CuO films.

CO_2 sensing characteristics were measured by the ac two-probe method. Specimens were set in a ceramic tube which was connected to a gas flow system. The CO_2 concentration in sensing gas was controlled by diluting commercial CO_2 with air which was always used as a reference gas in this study. The capacitance of the element was measured with an LCR meter (HIOKI type 3502) at 50 kHz. The sensitivity of the element was expressed by the ratio of the capacitance of CO_2 to that in air, C_{CO_2}/C_{air}.

EPR measurements were performed to determine the valence state of the template Cu in the bilayer film. Before measurement, the sample was evacuated for 1 h and EPR measurements were performed at room temperature in vacuum using a Bruker EPR 380 instrument. X-Ray absorption fine structure at the Cu K-edge was measured by a laboratory X-ray absorption system (TECNOS EXAC 820) with a Si (311) double crystal monochromator at room temperature in air. The source beam energy and current were 20 kV and 100 mA, respectively. The incident and transmitted X-rays were measured by using Ar charged ionization chambers and a semiconductor solid detector (SSD), respectively. The energy resolution (DE) was 3.6 eV and a single scan was collected. The photon energies were calibrated against characteristic pre-edge peaks in the absorption spectrum of Cu foil (8980 eV). The normalized spectra were obtained by procedures described by Tanaka *et al.*[14] and Fourier transformation was performed on k^3-weighted EXAFS oscillations in the range 0.3–1.2 nm^{-1} without any phase shift correction. Spectral simulation of EXAFS data was carried out using 'LABEXAFS' software (TECNOS) performed in a Unix box (Fujitsu S-4/CL-4). Fitting parameters were obtained from the theoretical equation based on a McKale spherical wave. The coordination number of Cu was fixed to four and the Debye–Waller term for the final fitting was 0.113 Å.



(a) DC1-16

(b) Modified ethylenediamine

Fig. 1 Scheme of dialkylammonium bromide (DC1–16) (a) and hexadecylethylenediamine (b) used for template molecules

3 Results and Discussion

3.1 Preparation of a molecular template of multibilayer film for CuO thin films

Fig. 2 shows the X-ray diffraction pattern of a resultant film on a glass substrate. It is obvious that diffraction peaks of the organic film suggest that the resultant cast film has a long-range order. The thickness of the bilayer film was estimated by using Bragg's Law with $n = 2$ for the diffraction peak at the lowest diffraction angle. By averaging d values estimated from each peak, the interplanar distance of the final film is found to be 6.96 nm. This interplanar distance should correspond to the thickness of the bilayer film consisting of DC1–16. Kimizuka and Kunitake also observed a similar XRD pattern on a bilayer film which was obtained by casting similar organic compounds and reported that the thickness of the bilayer film was 6.6 nm.[13] Therefore, it is considered that the cast film obtained here also consisted of a regularly assembled multibilayer film. Since the thickness of film obtained on a glass substrate by single casting is 78 µm by micrometer measurements, *ca.* 15 000 layers of the multibilayer film were estimated to be accumulated. The number of accumulated bilayer films can be changed by altering the concentration of DC 1–16 and in this study the number of accumulated layers were varied from 1000 to few 10 000 layers. This is one of the advantages of the casting method used throughout this investigation.

The valence state of Cu in the bilayer films was characterized by EPR, since Cu^{2+} is highly sensitive with respect to Cu by this technique. Fig. 3 shows the angular dependence of EPR spectra of Cu *vs.* magnetic field in the films. Clearly, a single peak which is assigned to Cu^{2+} is observed on cast films. Therefore, it is considered that Cu in the cast film is divalent. For highly dispersed Cu^{2+}, hyperfine structure is generally observed in the EPR signal.[15] However, only a single peak was observed in the case of the cast film. Absence of hyperfine structure is characteristic for EPR spectra of Cu^{2+} ions arranged in organic templates such as in LB film, despite the high dispersion state, and may be assigned to the interaction of Cu^{2+} with neighboring sites. On the other hand, the strength of the Cu^{2+} EPR peak decreased with increasing the incidence angle of the magnetic field. A similar dependence of the Cu^{2+} EPR signal on the incidence angle of magnetic field is also reported by Kimizuka *et al.*[16] on a similar bilayer film. Since the double integral of the Cu^{2+} EPR signal monotonously decreased with increasing the incident angle of the magnetic field as shown in Fig. 3(b), this suggests that Cu^{2+} ions are

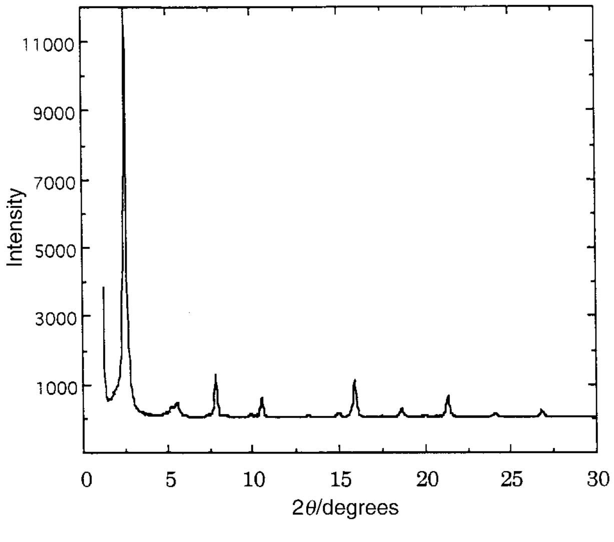


Fig. 2 X-Ray diffraction pattern of obtained casting film on a glass substrate; film thickness, 78 µm

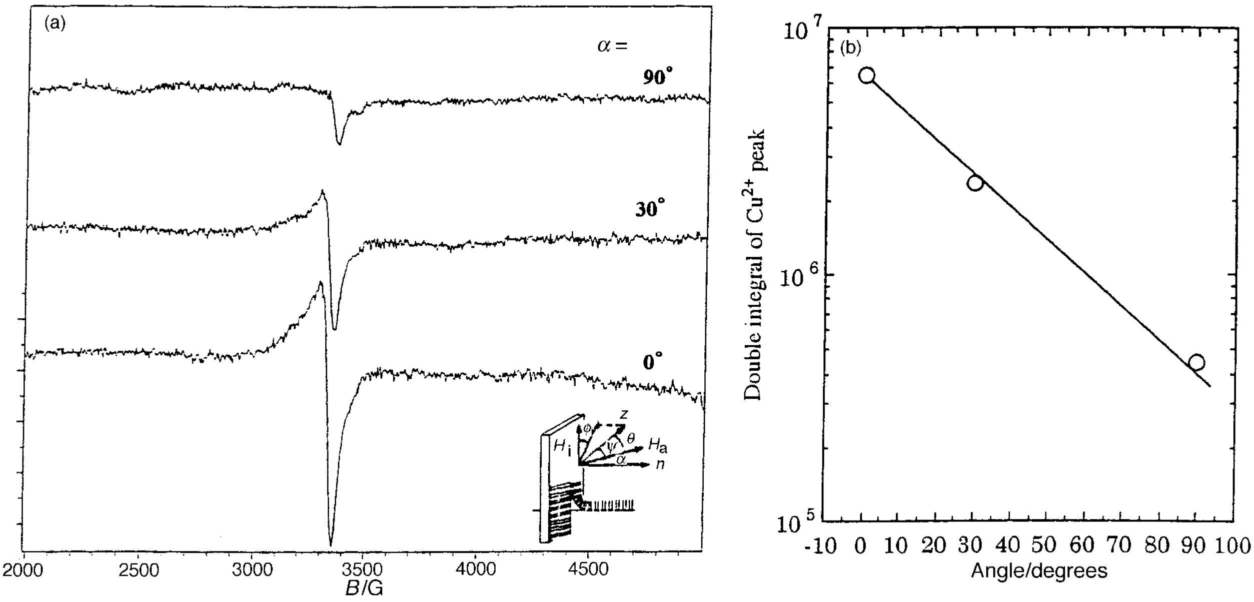


Fig. 3 EPR spectra and double integral of Cu in casting film as a function of incident angle of the magnetic field

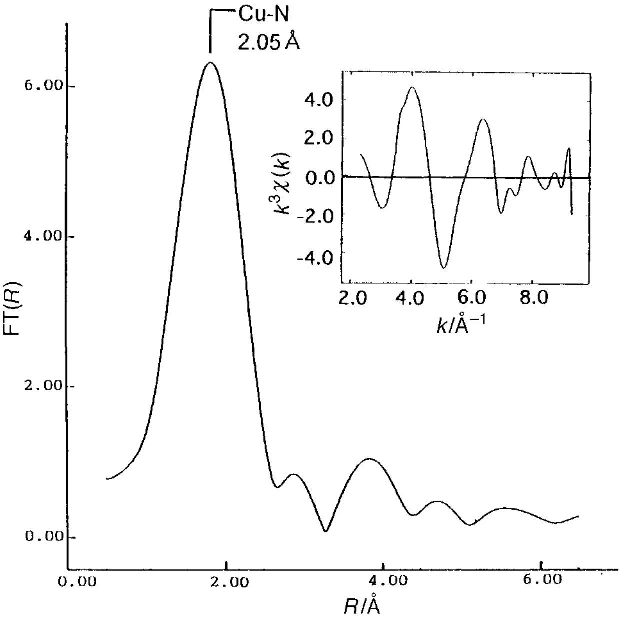


Fig. 4 Experimental Cu-K EXAFS and Fourier transform of Cu in the casting film

regularly arranged at the hydrophilic layer of the multibilayer film.[16,17]

To confirm that Cu^{2+} ions in the cast films are bonded to hexadecylethylenediamine, a ligand which fixes Cu^{2+} in the bilayer film, the local environment of Cu^{2+} was investigated by X-ray absorption spectroscopy. Experimental Cu K-EXAFS and Fourier transforms are shown in Fig. 4. Clearly, Fourier transforms are dominated by a single peak at 0.205 nm. Since no significant bands associated to Cu—Cu (*ca.* 0.33 nm) or Cu—C (*ca.* 0.29 nm) were observed in Fourier transforms of Cu K-EXAFS, copper ions seem to have no interaction with neighboring Cu ions in the cast film suggesting that the Cu^{2+} ions are isolated and dispersed at the atomic level. The parametric fit to the EXAFS spectra in Fig. 4 corresponds well with a Cu—N bond length which is reported for a cationic protein by Houser *et al.*[18] Therefore, it seems most likely that Cu^{2+} ions in the cast films are bonded by four nitrogen atoms of two hexadecylethylenediamine molecules.

Considering the results of EPR and EXAFS spectra, the structure of the resultant cast film is schematically shown in Fig. 5. Aqueous suspensions of DC1–16 lead to regularly assembled multibilayer films in spite of the simple casting procedure. In the multibilayer films, each Cu^{2+} ion is associated with four nitrogen atoms in two molecules of hexadecylethylenediamine which is fixed in bilayer films by long alkyl chains and thus Cu^{2+} is regularly and stably arranged in the hydrophilic layer of the molecular template. On the other hand, poly(vinyl alcohol) is hydrophilic and acts as a binder to maintain the regularity in the accumulated bilayer film.

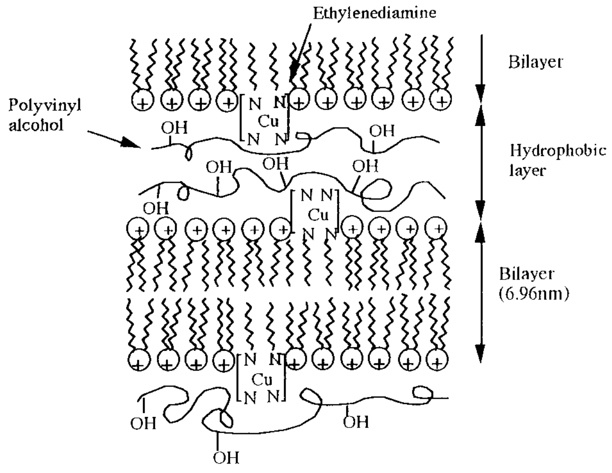


Fig. 5 Schematic of the structure of the obtained casting film

3.2 Removing the organic template by calcination

To obtain oxide films, 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 heat treatment in air. Calcination conditions of the cast film to obtain CuO thin films were also investigated. Fig. 6 shows the TG–DTA curve of DC1–16 powder. Some endothermic peaks without a significant weight loss were observed at temperatures lower than 373 K and one large exothermic peak with a large weight loss appears at temperatures from 473 to 673 K. Furthermore, two exothermic peaks with no corresponding weight loss were observed at temperatures higher than 673 K. The endothermic peaks at temperatures lower than 373 K appear to be assignable to a

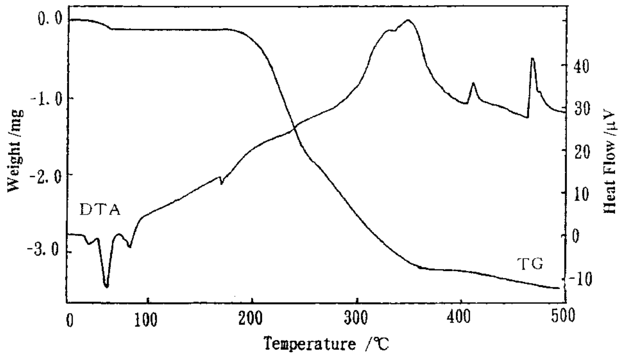


Fig. 6 TG–DTA curves of DC1–16

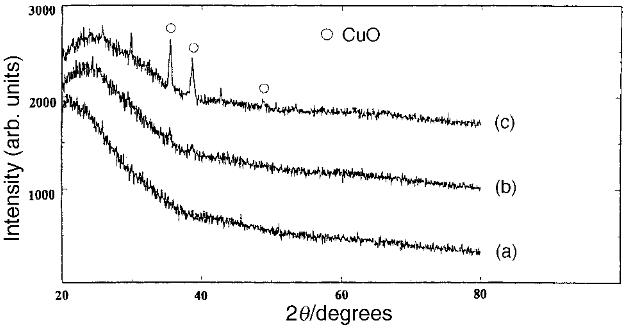


Fig. 7 XRD pattern of calcined films at (a) 673, (b) 723 and (c)773 K

phase transition of DC1–16. On the other hand, the exothermic peaks around 573 K correspond to the combustion of DC1–16. Consequently, it is essential to rapidly heat the cast film to a temperature higher than 523 K to obtain a uniform CuO thin film without destroying the ordered multibilayer film. Fig. 7 shows the XRD patterns of a film after firing at 673, 723 and 773 K for 6 h. Although weak diffraction peaks from CuO were observed for films after firing at 723 K, they become more significant after calcination at 773 K. Therefore, calcination of the cast film at temperatures higher than 723 K is essential to obtain a CuO film. The average CuO particle size is estimated by the line broadening method to be as low as 21 nm, and consequently, it became clear that decomposition of the cast film containing regularly arranged Cu^{2+} ion is effective to obtain a uniform and fine CuO film consisting of small particles. It is also noted that carbon and other impurities in the resultant CuO film were almost negligible according to XRF analysis. Therefore, the organic template can be completely removed by the proposed heat treatment resulting in high purity CuO films.

3.3 CO_2 sensing characteristics of CuO films prepared on $BaTiO_3$ by the template method

In our previous study, it was found that the capacitance at the grain junction between CuO and $BaTiO_3$ was sensitive to CO_2.[10] It is expected that the CO_2 sensitivity will be increased by decreasing the particle size, since the number of junctions of CuO and $BaTiO_3$ are increased. Fig. 8 shows the XRD pattern of a CuO film prepared on the porous $BaTiO_3$ substrate. The resultant CuO film was obtained by removing the organic film at 523 K followed by calcination at 1173 K for 1 h. Precalcination was performed to prevent lamination of the film during the quick heating. It is obvious that the XRD pattern of the resulting film consisted of diffraction peaks only from CuO and the $BaTiO_3$ substrate and consequently, no reaction products of CuO and $BaTiO_3$ were detected. Thus CuO thin films consisting of fine particles can be also prepared on a porous $BaTiO_3$ substrate by removing the assembled bilayer film, as well as on a glass substrate.

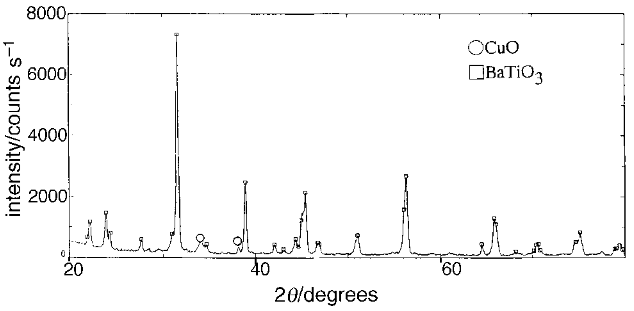


Fig. 8 XRD pattern of CuO film obtained on $BaTiO_3$ after combustion of the organic template at 523 followed by 1173 K

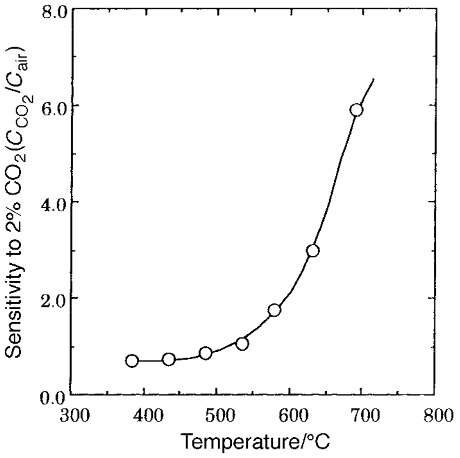


Fig. 9 Sensitivity to 2% CO_2 on $CuO/BaTiO_3$ as a function of temperature; measurement frequency, 50 kHz

Fig. 9 shows the CO_2 sensing characteristic of a CuO thin film on a $BaTiO_3$ substrate. Since the thickness of the resultant CuO film is not sufficient after a single casting, five consecutive castings were required. CuO films on $BaTiO_3$ substrates prepared by using self-assembled multibilayer films as precursors are denoted as $CuO/BaTiO_3$ in the following. The capacitance of the $CuO/BaTiO_3$ element increased upon exposure to CO_2, similarly to that of a powdered mixture of CuO and $BaTiO_3$. This also confirms that the interface between CuO and $BaTiO_3$ is important to detect CO_2 on a mixed oxide CuO–$BaTiO_3$ capacitor. Sensitivity to 2% CO_2 on the $CuO/BaTiO_3$ element monotonously increased with increasing temperature and attained a maximum value of 6.1 at 973 K. For a powder mixture of CuO and $BaTiO_3$, the maximum sensitivity was 2.8 at 755 K.[9] Therefore, the sensitivity of the element is twice as high on the $CuO/BaTiO_3$ element prepared from self-assembled multibilayer films. Since the capacitance of CuO thin films on $BaTiO_3$ substrates did not increase on exposure to CO_2 when the CuO film was prepared with a sputtering method, improved sensitivity of CuO films on $BaTiO_3$ substrates may be related to the porous structure of CuO films formed from the self-assembled multibilayer films. However, it is clear that preparing CuO thin films from self-assembled multibilayer films as precursors is effective in improving the sensitivity to CO_2 of a capacitive type CuO–$BaTiO_3$ sensor. Although the highest sensitivity was attained at 973 K which is the highest temperature measured, an operating temperature of 973 K is excessively high to sustain a stable response to CO_2. Therefore, it is considered that the optimized operating temperature for the $CuO/BaTiO_3$ element is around 873 K and the CO_2 sensing property at that temperature was measured in further detail.

The sensitivity of the sensor at 873 K is shown in Fig. 10 as a function of CO_2 concentration. The capacitance of the element increased with increasing CO_2 concentration over five orders of magnitude, *i.e.*, from 100 ppm to 50%. Consequently,

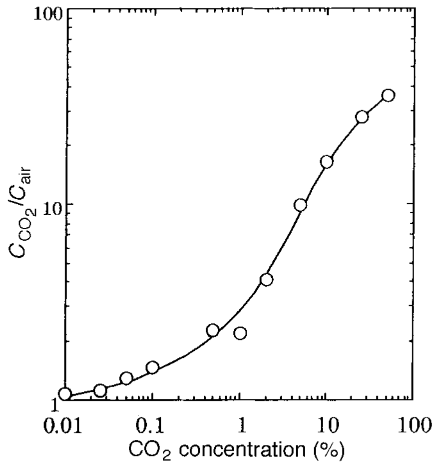


Fig. 10 Sensitivity of $CuO/BaTiO_3$ at 873 K as a function of CO_2 concentration; measurement frequency, 50 kHz

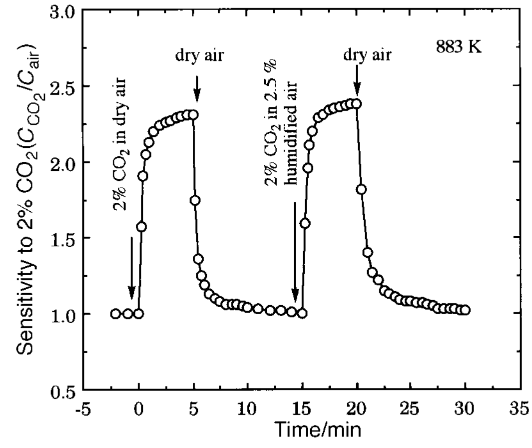


Fig. 12 Effect of humidity on the sensitivity to 2% CO_2 on a CuO/ $BaTiO_3$ capacitor at 883 K

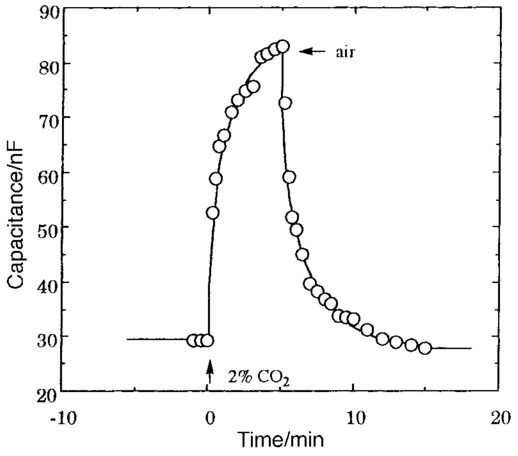


Fig. 11 Response curve to 2% CO_2 on $CuO/BaTiO_3$ at 873 K

CO_2 concentration can be estimated from the capacitance of the $CuO/BaTiO_3$ element prepared by combustion of self-assembled bilayer films. For the oxide mixture of CuO–$BaTiO_3$, detectable CO_2 concentrations ranged from 30 ppm to 5%. Therefore, in this study, the lower limit of detectable CO_2 concentration was improved by three times whereas the upper limit was greatly increased on the $CuO/BaTiO_3$ element. This may be related to the increased operating temperature. On the other hand, the calibration plot in Fig. 10 was slightly curved. In contrast to the simple calibration curve of solid electrolyte type sensors, a slightly complicated calibration equation will be required for estimating CO_2 concentration on this capacitive type sensor.

The capacitance of the $CuO/BaTiO_3$ element shows a good reproducibility to the response on exposure to CO_2. Fig. 11 shows the response characteristics of $CuO/BaTiO_3$ to 2% CO_2 at 873 K. The period for 80% response and recovery was 108 and 118 s, respectively. By contrast, the oxide mixture of CuO and $BaTiO_3$ exhibited a rapid response to CO_2 and the 80% response was attained within 25 s. However, it takes a long time to recover to the original level (80% recovery period = 180 s). Therefore, the response time was longer but the recovery period was shorter for the $CuO/BaTiO_3$ element. The prolonged response time may be caused by the enlarged capacitance change and high operating temperature of the CuO/ $BaTiO_3$ element. On the other hand, the increased operating temperature seems to shorten the period for recovery. This is because the chemical equilibrium generally shifts towards desorption with higher temperature. Therefore, it is reasonable that the response and the recovery period became longer and shorter, respectively, by increasing the operating temperature. However, it is considered that the $CuO/BaTiO_3$ element exhibits reasonable response characteristic as a CO_2 sensor for monitoring an indoor atmosphere, since the indoor CO_2 concentration changes only slowly.

For a CO_2 sensor, not only a high sensitivity but also a high selectivity to CO_2 are required, since CO_2 is a highly stable molecule. In particular, high stability towards humidity and absence of interference by humidity are also required. As reported previously, CuO mixed with $BaTiO_3$ is negligibly influenced by humidity.[8] Fig. 12 shows the influence of humidity on the sensitivity of $CuO/BaTiO_3$ to 2% CO_2. It is obvious that the sensitivity as well as the response time were scarcely affected by 2.5% humidity which corresponds to saturated water vapor pressure at room temperature. Although the influence of coexisting gases should be further investigated in detail, it can be stated that $CuO/BaTiO_3$ sensors are highly selective towards CO_2. The negligible influence of humidity seems to be attributed to a low adsorption of water due to the high operating temperature of 883 K. For practical application of this capacitive type sensor, long term stability should be measured (*e.g.* over a year). However, it can be concluded that the preparation of CuO thin films on $BaTiO_3$ *via* self-assembled multibilayer films as a molecular template is effective for improving the sensitivity to CO_2, since the capacitance of $CuO/BaTiO_3$ reproducibly responds to CO_2.

4 Conclusion

Preparation of CuO thin films *via* self-assembled multibilayer organic films was investigated to prepare CuO thin films for capacitive type CO_2 sensors. Bilayer films of a few 1000 layers were self-assembled by casting aqueous suspensions of dimethyldidodecylammonium bromide (DC1–16). Furthermore, it is observed that Cu^{2+} ions are arranged in atomic scale regularity in the hydrophobic part of multibilayer films by using hexadecylethylenediamine. CuO thin films were obtained by the removal of the self-assembled multibilayer film by heat treatment. Since the resulting CuO thin films consisted of fine and uniform sized particles, such films on $BaTiO_3$ exhibited a high sensitivity towards CO_2. From this point of view, preparation of inorganic film by oxidizing cations arranged with atomic level regularity is an attractive method for the preparation of useful materials for gas sensors.

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