Mass-Producible CuBr Thick Film Gas Sensors and its Highly Selective Ammonia Sensing Properties

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***Abstract*— Prototype copper (I) bromide (CuBr) thick film ammonia sensors were fabricated by a simple painting process and those gas sensing properties at room temperature were evaluated. These sensors showed performance comparable to the highly sensitive and highly selective CuBr thin film sensors in the literatures. The sensor is expected to be the first mass-producible commercial CuBr sensor since this can be manufactured in the same way as our commercial MEMS metal oxide semiconductor sensors.**

Keywords*— *gas sensor, copper bromide, ammonia, environmental monitoring

I. Introduction

Since the report published early in 21st century [1], copper (I) bromide (CuBr) has been known as a gas sensitive material that reacts with ammonia selectively at room temperature. Although not as well-known as metal oxide semiconductor (MOS) type sensors, CuBr sensors have extremely high selectivity for ammonia compared to them [2]. Many attempts like adding a catalyst layer on the surface, loading noble metal, and forming sensor-array have been performed to possess selectivity for MOS sensors [3], however, these approaches usually result in still insufficient of selectivity, raising the detection limit of ammonia, and increasing unit cost. In this respect, CuBr sensors show excellent selectivity with a single sensor element because they utilize the change in electric conductivity of the sensing material (CuBr) accompanying the inherent complex formation reaction between ammonia and copper ions for gas detection [4].

Possible application of ammonia sensors includes non-invasive health diagnosis by breath analysis, odor monitoring, and protection of artworks from degradation in the museum are expected. Under such circumstances, MOS sensors have long been highly anticipated since they are known as inexpensive, mass-producible and highly sensitive gas sensors. However, most MOS sensors for ammonia detection suggested before suffer from difficulties in gas selectivity and no practical-level sensors are yet commercialized. Whereas electrochemical ammonia sensors with sufficiently high reliability and gas selectivity are expensive (generally several times more expensive than MOS sensor) and do not have a resolution of tens of ppb detection. Amongst those sensors, CuBr ammonia sensors have the same advantages of above-mentioned two types of sensors while they have a lower limit of detection. The issue is that the manufacturing methods of CuBr sensors employed in the previous reports are not suitable for mass production. As discussed later, the major drawback of this sensor is its short lifespan. Those have prevented its commercialization to date.

In this paper, we first show the gas sensing properties of CuBr thick film sensors prepared by a painting process. This method has an advantage that it can easily progress to mass production. The performance of these sensors demonstrated to be comparable to those in the literature. This fact shows that we have paved the way for the first commercial CuBr ammonia sensor.

II. Experimental

Most of the methods employed in the literatures to fabricate CuBr sensors, such as sputtering [1], thermal evaporation [5], and flame spray pyrolysis [6], require expensive equipment such as vacuum systems and stainless steel chambers. If the metal halide thin films are prepared using the above methods, there is a high possibility of corrosion damage from bromine gas in the exhaust system. The authors first carried out a trial fabrication of CuBr thin film sensors by adopting a manufacturing method developed by Fujitsu Laboratories Ltd [7]. In this method, firstly the preparation of the copper seed layer is carried out in a dry process. The layer is subsequently grown to copper bromide by immersion into a $CuBr_2$ methanol solution. With this method, no damage to the equipment caused by bromine gas occurs. Manufacturing with low-cost is also important for the commercialization of CuBr sensors since it shows short lifespan. Reddy et al [8] reported CuBr thick film carbon monoxide sensor fabricated by the painting process. We also attempted to obtain CuBr thick film sensors by slurrying CuBr powder and formed it on alumina substrates with platinum electrodes. The commercially available CuBr powder was slurried with an appropriate organic solution and was painted on the substrates, following by sintered at 300 °C for 1 h. This is a typical method author's group have employed for a long time to mass-produce MOS sensors [9].

III. Results and Discussion

A. CuBr thin film sensors

The response of a CuBr thin film sensor produced by bromination of copper thin films by a liquid phase process to ammonia is shown in Fig. 1. The operating temperature was set at room temperature. The rate of change in resistance R_s/R_0

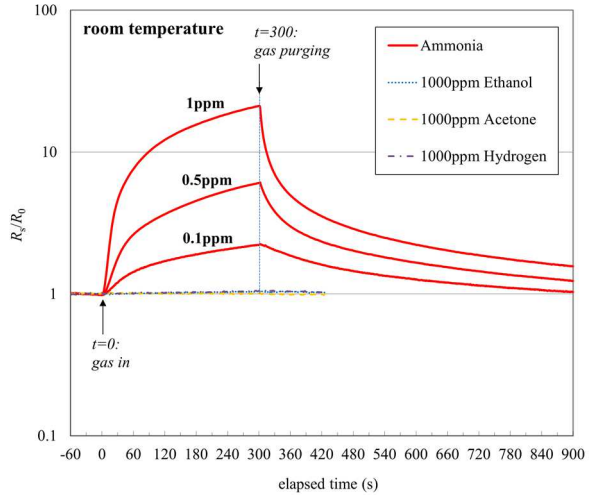

Fig. 1. The gas responses of CuBr thin film sensor. R_0=15.7(kΩ)

is used as sensitivity of the sensor, where R_0 is the stable electric resistance in room air and R_s is the resistance in the analyte gas. Gas exposures were conducted in a stainless steel chamber of 20 L capacity, with background indoor-air at relative humidity (RH) of 50 %. As in the literatures, the sensor showed a sufficiently high sensitivity to 1 ppm ammonia at room temperature, with R_s/R_0=21.2 at t=300 s, while showing almost no responses to VOCs and hydrogen. In a similar way, the interferences with substances expected to coexist with ammonia in various applications were assessed. Results are shown in TABLE I. In this table, "NH_3 equivalent" stands for the concentration of ammonia that has the same R_s/R_0 value as the R_s/R_0 value when exposed to the analyte. CuBr sensor proved to be immune to VOCs and combustible gases, to which MOS sensors generally show a large response. However, CuBr sensor showed responses to some components - especially hydrogen sulfide, acetic acid and oxidizing gases. Weak changes in resistances to hydrogen sulfide and acetic acid are considered to be due to the same reaction with the ammonia and CuBr, i.e. those gas molecules form complexes by coordinating with copper ions. The reason for the inverted responses (decrease in resistance) upon exposure to oxidizing gases is considered to be due to the injection of holes when they adsorb to the *p*-type CuBr surface, causing an increase in electrical conductivity.

As a practical sensor, the evaluation of lifespan is important. Since CuBr is a nonoxide material, it is destined to be deactivated in a relatively short period due to copper oxidation in the atmosphere. Therefore, the product lifespan of CuBr gas sensors must be significantly inferior to that of MOS sensors (generally 1-5 years). Fig. 2 shows the results of the lifespan evaluation of CuBr thin film sensors under different conditions. In this figure, each initial R_s/R_0 values are normalized to 1. Fig. 2(a) shows the case where the sensor is left indoors (50% RH) without energizing. Sensitivity to ammonia in the sub-ppm region, which is a strong advantage of this sensor, was lost in one week. Fig. 2(b) shows the case where a bias voltage was constantly applied to keep the sensor ready for sensing. Sensitivity was also lost in an even shorter period. The constant migration of copper ions can be considered a cause of this rapid degradation. Little is known about the detailed process of CuBr alteration in the atmospheric air, but it is empirically known that the alteration is accelerated by humidity. Fig. 2(c) shows the case where the sensor was stored in a container kept below 10% RH at all times while no measurements were made. It was confirmed that the sensitivity to sub-ppm ammonia could be maintained for at least 50 days with this storage method.

TABLE I. LIST OF INTERFERENCES AND NH_3 EQUIVALENT

Analyte	Concentration	NH_3 equivalent
Ethanol, IPA, Toluene, Acetone, Methanol	1000 ppm	< 1ppb
Hydrogen	1000 ppm	< 1ppb
Carbon dioxide	5000 ppm	< 1ppb
Ozone*	0.8 ppm	218ppb
Hydrogen chloride*	3.2 ppm	134ppb
Hydrogen fluoride	3.2 ppm	< 1ppb
Hydrogen sulfide	0.1 ppm	19ppb
Sulfur dioxide*	0.1 ppm	< 1ppb
Acetic acid	0.1 ppm	60ppb

* inverted response

B. CuBr thick film sensors

If the sensor element is necessarily disposable in a short period (e.g. replace every 1-2 month(s)), the most prioritized factor for a sensor is likely to be low unit cost. CuBr thin film sensors mentioned above are manufactured by two step thin film growth processes. Although this technique has the sufficient potential for mass production, but is estimated to be difficult to suppress the cost because it requires expensive equipment. Authors believe that the method for manufacturing CuBr thick film sensors proposed here is the method with the easiest and therefore the lowest cost amongst reported so far.

Fig. 3. shows the response of a CuBr thick film sensor to ammonia and VOCs at room temperature. The sensor showed a very large R_s/R_0 to 50 ppb ammonia while it is almost immune to ethanol and acetone. Surprisingly, the response of the thick film sensor to ammonia is even larger than that of the thin film sensor. The main reason for this is considered to be that the sintering process removes the contamination that remains in the thin film type, where no heat treatment is carried out.

In addition to ethanol and acetone, the same interfering gases as in TABLE I were evaluated for the thick film type. Results were almost similar to those of the thin film type. This result mean that the high selectivity was maintained for this thick film type. The lifespan of the thick film sensors were also at the same level or longer than that of the thin film sensors shown in Fig.2(c). Stable sensitivity to ammonia for more than two months can be achieved when the sensors are stored in a dehumidified environment during standby.

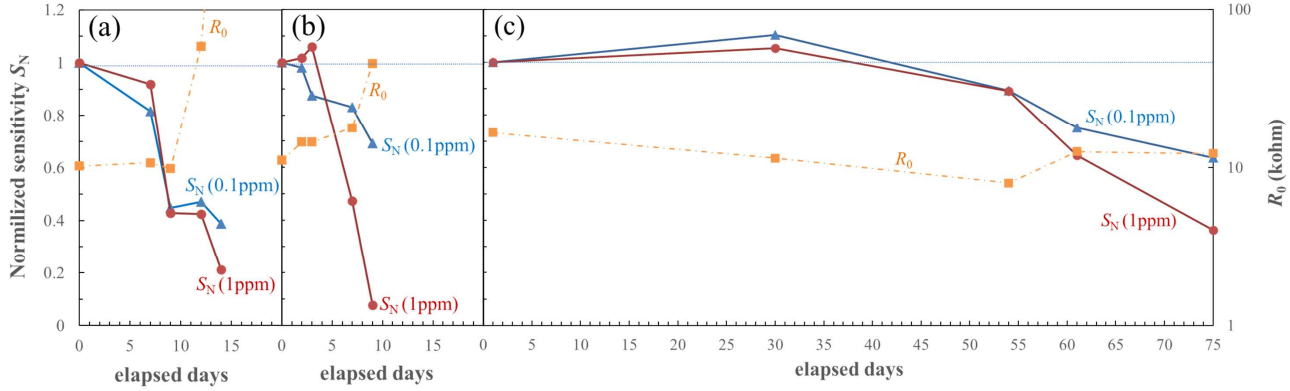

Fig. 2. Temporal variation of the ammonia response and element resistance of CuBr thin film sensors. (a) left in the indoor room without energization, (b) continuously energized in the indoor room, (c) stored in low humidity (<10% RH) except when measuring gas response.

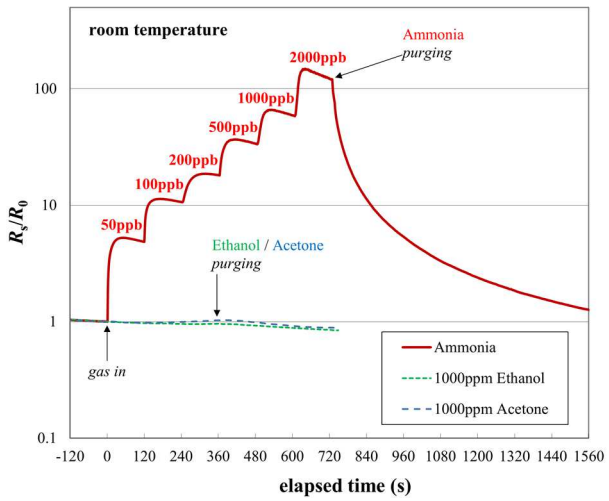

Fig. 3. The gas response of CuBr thick film sensor. R_0=2.3(kΩ)

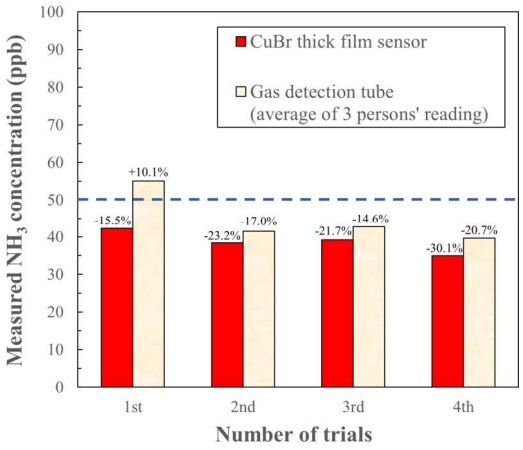

Fig. 4. Comparison between CuBr thick film sensor and detector tubes.

C. *Comparison with detector tubes*

Currently, the most inexpensive and simple method to measure ammonia concentrations at sub-ppm levels is using detector tubes. In order to evaluate the performance of CuBr thick film sensor as a detector of sub-ppm ammonia gas, a comparison of concentration measurement results with a detector tube has been performed. The 900 NHH ammonia detector tube (Komyo Rikagaku Kogyo Co., Ltd.) was used for comparison. Ammonia gas was adjusted to a concentration of 50 ppb in a gas bag made of poly vinylidene fluoride (PVDF) with nitrogen as background gas. To measure the ammonia concentration using the CuBr thick film sensor, a calibration curve was generated in advance from R_s/R_0 values for several known concentrations of ammonia. The concentration was then estimated by measuring the R_s/R_0 values when the ammonia gas in the PVDF bag was aspirated. When measuring the ammonia concentration in the bag, the sensor was placed in a small container. The analyte gas was aspirated at 1.5 L/min from the outlet side of the container using a diaphragm pump and exposed to the sensor surface. For the detector tube, the analyte gas was aspirated at a rate of 400 ml/min for 60 min according to the instructions for use. To verify reproducibility, identical experiments were conducted once a day on four different days. Since individual variations occur in the reading of the detector tube's indication, the readings were taken from any three persons (who are uninformed the concentration of analyte). Each average value was treated as the concentration value of the detector tube.

The results are shown in Fig.4. The tolerance of the detector tube is specified as ±25 % [10], and all four measurements were within this range. The ammonia concentrations estimated by the CuBr thick film sensor were within -25 % three out of four times. This result means that the accuracy of the CuBr thick film sensor is comparable to that of the detector tube. As the analyte gas was low-concentration ammonia, which may have caused adsorption of gas molecules on the inner surface of the gas bag. Hence, the actual accuracy could be higher in both cases.

IV. Conclusion

CuBr thick film ammonia sensors were fabricated and those gas sensing properties at room temperature were evaluated. The results showed that the CuBr thick film sensors have high sensitivity and high selectivity to ammonia comparable to those of the thin film type sensors in the literatures. Lifespan evaluation revealed that the CuBr sensors lost their sensitivity within a few months. This fact indicates that the CuBr sensors are likely to be disposable. In which case the thick film sensors proposed in this paper is very advantageous due to its quite low production cost. The authors group holds production line which is already in operation for automated mass production of commercial MEMS MOS sensors [11]. Thus, the authors believe that the first commercial CuBr sensors will be realized using this mass-production method in the near future.

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