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Combined effects of small gold particles on the optical gas sensing by transition metal oxide films

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Abstract

The combination of small Au particles with NiO, CuO and Co_3O_4 films led to improved or new optical gas sensitivity via different mechanisms. The deposition of small Au particles on NiO film enhanced the detection of CO in air through a decreasing change of absorbance in the whole visible–near IR region. This can be explained by the change in positive hole density change of NiO, which was enhanced by an increase in catalytic formation and decomposition of surface carbonates with Au. In the case of CO-insensitive CuO film, gold deposition made it sensitive only at plasmon absorption region. This might be because the absorbance by small Au particles in plasmon band was influenced by the change in the dielectric constant of copper oxide which surrounded small Au particles. A Au–Co_3O_4 composite film showed a novel function to recognize CO and H_2, probably for the first time as inorganic materials for optochemical sensors. This owes to the fact that CO and H_2 bring about the specific absorbance change of the film at different wavelengths. Carbon monoxide decreased the absorbance of Co_3O_4 moiety, while H_2 not only decreased the absorbance of Co_3O_4 moiety but also increased plasmon absorbance of Au.

Keywords: Optochemical sensors; Absorbance change; Transition metal oxide films; Gold particles (small)

1. Introduction

Materials whose optical absorption properties are reversibly modified by atmospheric gases have considerable potential for use of optochemical sensors [1,2]. The advantages of optochemical sensors over conventional electricity-based gas sensors are higher resistivity to electromagnetic noise, compatibility with optical fibers and the potential of multi-gas detection using differences in the intensity, wavelength, phase and polarization of the output light signals.

During the course of a study on the gas sensing properties and catalysis of a variety of transition metal oxides with and without Au deposition, we have found that they are applicable to optical gas sensing [3–7]. The phenomenon found in the beginning was that thin films of NiO, Co_3O_4 and Mn_3O_4 showed reversible decreases in the visible–near IR absorption due to CO at temperatures around 250–350°C [3]. This absorbance change was assumed to be correlated with a change in positive hole density during catalytic CO oxidation. Several years later, the combination of small Au particles to NiO film [4,5] and to CuO film [7] has been proven to be effective to enhance or create the optical sensitivity to CO. Furthermore, when small Au particles were combined with Co_3O_4,

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a new function to recognize CO and H_2 was created [6]. The gas-sensitive optical absorption properties are significantly different between Au–NiO, Au–CuO and Au–Co_3O_4 films, however, the mechanism was not satisfactorily clarified yet. In the present paper, we try to compare the gas sensing characteristics of the Au–NiO, Au–CuO and Au–Co_3O_4 films and to discuss the difference in sensing mechanism based on the reaction pathways for CO or H_2 oxidation.

2. Experimental

Thin films of transition metal oxides of several tens nm thick were prepared by pyrolysis (380°C) of transition metal alkylcarboxylates spin-coated on glass plate substrate (18 mm × 18 mm × 0.1 mm) from organic solution [3,6,8].

Gold-transition metal oxide composite films were prepared in the following two manners.

Method 1: Small Au particles were deposited directly on a glass plate substrate by d.c. sputtering method [6,7]. The amount of deposited Au was estimated to correspond to that of a continuous Au film of approximately 2 nm thick. Transition metal alkylcarboxylate was then spin-coated on the highly dispersed small Au particles on a glass plate substrate, and pyrolyzed at 380°C [3,6–8].

Method 2: Gold hydroxide was deposited on the transition metal oxide film from a neutralized aqueous solution of $HAuCl_4$ at 70°C. The film was then washed, dried and calcined at 300°C in air (deposition–precipitation method) [5,9].

The thickness of transition metal oxide layer in each composite film was estimated by a Mizojiri DHA-XA2 ellipsometer.

Electron microscopy showed that the composite films prepared by methods 1 and 2 consist of small Au particles and small crystals of transition metal oxides with sizes ranging from several nm to several tens nm.

Visible–near IR absorption spectra (λ = 400–1700 nm) of the films were measured in a quartz cell (200 ml) filled with the controlled atmospheric gas with a Shimadzu UV-3100PC spectrometer equipped with optical fibers. The temperature of the quartz cell was controlled in the range of 150–300°C. Test gases were fresh air (atmospheric dry air without the addition of CO or H_2) and dry air containing CO or H_2, and were passed through the quartz cell at a constant flow rate of 100 ml/min. All gases were dried by passing through silica gel and molecular sieve columns at room temperature and a molecular sieve column at 0°C prior to use. Film samples were pretreated at the operating temperature in fresh air for at least 1 h before measurements were made.

3. Results

3.1. Enhancement of optical CO sensitivity in Au–NiO composite films

The thickness of NiO layer in the Au-free NiO film and Au–NiO composite film was estimated to be about 85 nm. Gold–nickel oxide composite films prepared by methods 1 and 2 resulted in the similar enhancement of the optical CO sensitivity [4,5].

In the absorption spectrum of the Au–NiO composite film, dipolar plasmon excitation of

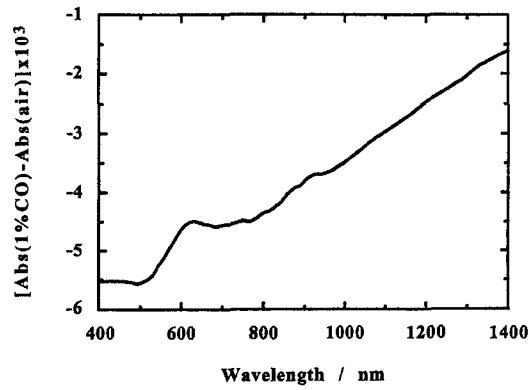

Fig. 1. Absorbance change (ΔAbs) of Au–NiO composite film caused by 1 vol.% CO in air as a function of wavelength. Temperature: 175°C.

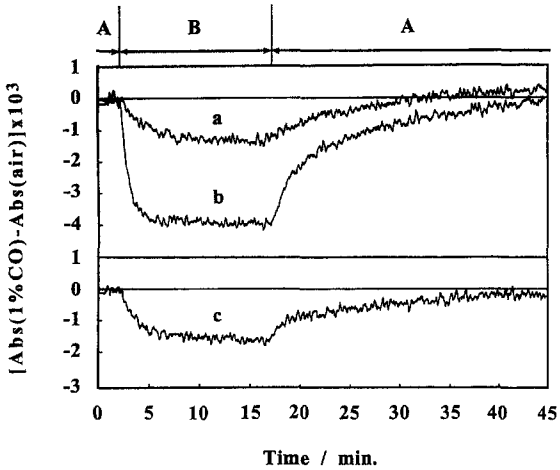

Fig. 2. Absorbance changes of NiO film and Au–NiO composite film as a function of time under atmosphere periodically changing from air (A) to air containing 1 vol.% CO (B): (a) NiO film at 175°C; (b) Au–NiO film at 175°C; (c) Au–NiO film at 150°C. Wavelength: 900 nm.

small Au particles [10] was observed with a maximum at a wavelength of around 600 nm as well as a broad absorption band due to NiO in the whole visible–near IR region.

Fig. 1 shows the CO-sensitive absorbance change (ΔAbs) of the Au–NiO film as a function of wavelength at 175°C. The presence of carbon monoxide in air appreciably reduced the absorbance of the film over the whole visible–near IR region. ΔAbs of the Au–NiO film was slightly suppressed in the plasmon band at around 600 nm compared with those in other wavelength region, probably due to the light absorption by the surface plasmon of Au at the Au–NiO interface [4,5,11].

Fig. 2 shows the response curves of the absorbance change due to CO at a wavelength of 900 nm for the NiO film and the Au–NiO composite film at 175°C and at 150°C. It is seen that the combination of Au with NiO films enhanced both the CO-sensitive ΔAbs and the response rate. At 175°C, the CO-sensitive ΔAbs was about 3 times enhanced by combining Au. No absorbance change was detected at 150°C for the Au-free NiO film, while the Au–NiO composite film showed reversible absorbance changes even at temperatures below 150°C. This indicates that the temperature for operation as an optical CO sensor can be lowered by combining Au. For both Au-free NiO film and Au–NiO composite film, CO-sensitive ΔAbs and response rate increased with increasing operating temperature from 150 to 250°C [5]. The CO-sensitive ΔAbs decreased with decreasing CO concentration [5], however, for Au–NiO film operated at 200°C, ΔAbs by 100 ppm CO was detectable and was about 29% of that by 1 vol.% CO.

Decrease of absorbance was also caused by H_2 with similar wavelength dependence and similar ΔAbs to those by CO.

3.2. Optical detection of CO by the plasmon absorption of Au–CuO composite films

The thickness of CuO layer in the Au-free CuO film and Au–CuO composite film prepared by method 1 was estimated to be about 35 nm.

In the absorption spectra of the Au–CuO film, there is a strong absorption band with a maximum at around 600 nm of wavelength, which is not observed in the absorption spectrum of a Au-free CuO film. This absorption band can be ascribed in a large part to the dipolar plasmon excitation of small Au particles [10]. Neither a Au-free CuO film nor pure small Au particles deposited on a glass plate substrate

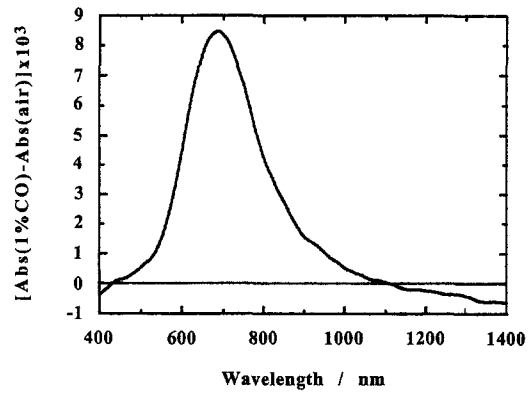

Fig. 3. Absorbance change (ΔAbs) of Au–CuO composite film caused by 1 vol.% CO in air as a function of wavelength. Temperature: 225°C.

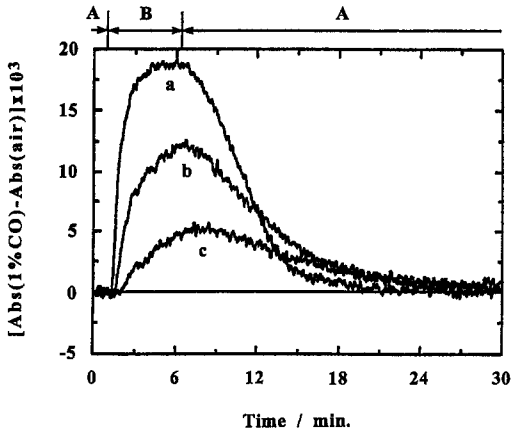

Fig. 4. Absorbance changes of Au–CuO composite film as a function of time under atmosphere periodically changing from air (A) to air containing 1 vol.% CO (B): (a) at 300°C; (b) at 250°C; (c) at 225°C. Wavelength: 700 nm.

by d.c. sputtering showed any detectable absorbance change in the presence of CO. In contrast, the Au–CuO film showed an increase in absorbance due to CO. This suggests that a synergistic effect brought about the optical CO sensitivity of the Au–CuO film [7].

Fig. 3 shows the CO-sensitive absorbance change (ΔAbs) of the Au–CuO film as a function of wavelength at 225°C. In contrast to the Au–NiO film, CO increased the absorbance of the Au–CuO film. There is an appreciable wavelength dependence in ΔAbs. An increase in absorbance occurred in a limited wavelength region near the plasmon band of Au. The ΔAbs by 1 vol.% CO was largest at a wavelength of 688 nm, while the peak wavelength of the Au plasmon band in air was 598 nm at 225°C. This implies that the Au plasmon band slightly shifted to the longer wavelength region upon being exposed to CO.

Fig. 4 depicts the response curves of the absorbance change due to CO at different operating temperatures for the Au–CuO film. The CO-sensitive ΔAbs could be observed as a reversible one at temperatures above about 175°C. ΔAbs and the response rate increased with increasing operating temperature from 175 to 300°C. The CO-sensitive ΔAbs decreased more appreciably with a decrease in CO concentration [7] than that for the Au–NiO film, however, because the absolute value of ΔAbs is large, ΔAbs by 100 ppm CO was still detectable and was about 17% of that by 1 vol.% CO at 300°C.

The increase of absorbance was also caused by H_2 with similar wavelength dependence to that by CO, however, ΔAbs by 1 vol.% CO was 3 times larger than that by 1 vol.% H_2.

3.3. Optical recognition of CO and H_2 by use of Au–Co_3O_4 composite films

The thickness of Co_3O_4 layer in the Au-free Co_3O_4 film and Au–Co_3O_4 composite film prepared by method 1 was estimated to be about 60 nm.

Fig. 5 shows a transmission electron micrograph of the Au–Co_3O_4 composite film. Spherical Au particles (black circles) with diameters in the 10–40 nm range are well dispersed in the Co_3O_4 matrix (light color part) consisting of a number of ultrafine crystals with sizes of 5–10 nm [12].

In the absorption spectrum of the Au–Co_3O_4 composite film, were observed both the Au plasmon band with a maximum at a wavelength of about 600 nm and the broad absorption band of spinel-type Co_3O_4 in the whole visible–near IR region [6].

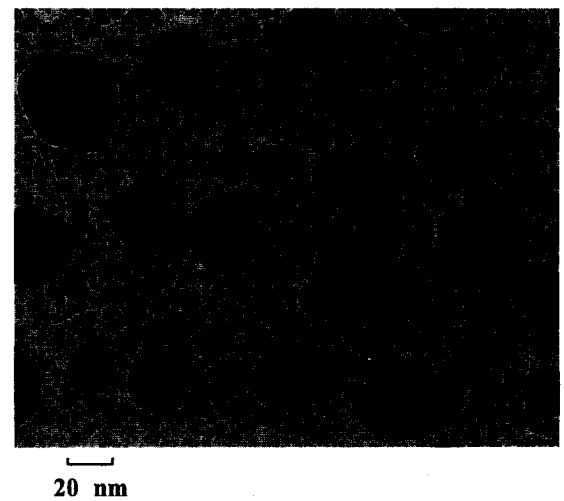

Fig. 5. A transmission electron micrograph of the Au–Co_3O_4 composite film (Taken by S. Iijima [12]).

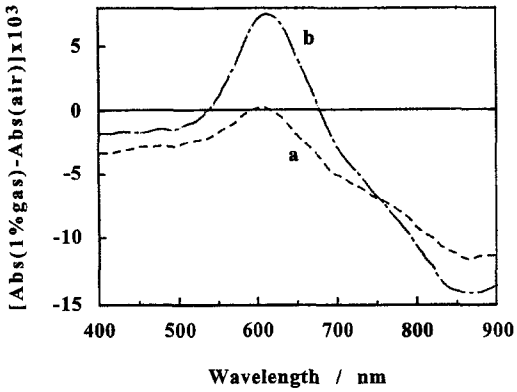

Fig. 6. Absorbance change (ΔAbs) of Au–Co_3O_4 composite film caused by 1 vol.% CO (a) and by 1 vol.% H_2 (b) in air as a function of wavelength. Temperature: 200°C.

Fig. 6 shows the wavelength dependence of gas-sensitive ΔAbs of the Au–Co_3O_4 film at 200°C. The absorbance was decreased by both CO and H_2 in the wavelength region outside the plasmon band of small Au particles, for instance, at $\lambda = 900$ nm. The decrease in CO- or H_2-sensitive absorbance at 900 nm for Co_3O_4 was enhanced by the combination with Au, which is similar to the enhancing effect in the Au–NiO film.

In the wavelength region around 600 nm, different behavior appeared between the optical response to CO and to H_2. The absorption peak of the Au–Co_3O_4 film was increased by H_2, but not by CO. This phenomenon reversibly occurred at CO or H_2 concentrations over the wide range. Small Au particles deposited on a glass plate substrate did not show detectable change of absorbance by CO nor by H_2 in air. Therefore, the peculiar behavior at around 600 nm is not explainable by a simple superposition of the spectrum for Co_3O_4 and that for small Au particles but by a synergistic effect between Co_3O_4 and Au. At both wavelengths of 600 nm and 900 nm, ΔAbs decreased with decreasing CO or H_2 concentration [12]. At a wavelength of 600 nm, ΔAbs by 100 ppm H_2 was about 15% of that by 1 vol.% H_2. At a wavelength of 900 nm, ΔAbs by 100 ppm CO and that by 100 ppm H_2 were about 39% and 13% of ΔAbs by 1 vol.% CO and that by 1 vol.% H_2, respectively.

Thus, it is possible to recognize CO and H_2 by monitoring the absorbance change at two different wavelengths, for instance, at 600 nm and 900 nm.

4. Discussion

The CO-sensitive decrease of the absorbance of the Au-free NiO film and of the Au–NiO film can be ascribed to a decrease of positive hole density in NiO due to a decrease in oxygen anion density on the surface of NiO during the catalytic oxidation of CO [3]. Oxygen molecules adsorb on the NiO surface as the activated oxygen anions and generate positive holes in NiO. When CO is added in air, the adsorbed oxygen anions are consumed by the catalytic oxidation of CO. The ΔAbs and response rate of the Au–NiO film were larger than those of the Au-free NiO film, which is assumed to be basically due to the enhanced catalytic activity for CO oxidation by the combination of Au [13,14].

However, even in the case of the Au–NiO composite film, much higher operating temperature was needed for the optical CO detection as compared with the operating temperature for the catalytic CO oxidation over small Au particles deposited on NiO powder, for example, −70°C [13]. This difference in the operating temperature between CO sensing and overall catalytic CO oxidation can be partly explained by the difference in the major reaction pathway for CO sensing and that for overall catalytic CO oxidation on the small Au particle–metal oxide composite systems. It is indicated by the studies on the Au–ZnO and Au–TiO_2 catalysts [15–17] that the reaction pathways for the optical CO sensing, that is, the CO-sensitive charge carrier density change, mainly consist of the formation and decomposition of carbonate-like species on the oxide surface. For example, the positive

hole density decreases when the following reaction takes place [16]:

$$CO + 2O^{2-} + 2Vo^{2+} \rightarrow CO_3^{2-} + 2Vo^{+},$$

where Vo^{2+} is a divalent oxygen vacancy and Vo^{+} is a monovalent oxygen vacancy.

This reaction is relatively slow and is accelerated only at temperatures above about 100°C. On the other hand, the reaction pathways for the overall catalytic CO oxidation is considered to involve the formation and decomposition of intermediate species like O≡C–Au = O on the Au sites at the Au-oxide perimeter. This reaction can take place even at temperatures below room temperature, down to −70°C. The present Au–NiO film started to show absorbance changes at the same temperature region (> 125°C) both to CO and to H_2, while the temperature for the overall catalytic oxidation of CO is much lower than that of H_2 over small Au particles deposited on NiO powder. For this Au–NiO powder catalyst, the temperatures for 50% oxidation of CO and of H_2 were < −70°C and about 70°C, respectively [13]. These temperature dependences support our present speculation in which the optical CO sensitivity may relate with the formation and decomposition of carbonate-like species on the oxide sites and optical H_2 sensitivity may relate with overall H_2 oxidation. The absorbance decrease by CO and by H_2 in the Au–Co_3O_4 composite film at wavelengths outside the Au plasmon band can be explained in the similar manner.

On the other hand, the CO-sensitive absorbance change in the Au–CuO film was not observed over the whole absorption band of CuO but observed only at wavelengths near the plasmon band of Au. This wavelength dependence and CO-insensitive absorbance of Au-free CuO film suggest that the CO-sensitive absorbance change of the Au–CuO composite film would be explained not by positive hole density change during surface reaction but by other mechanism which influences the plasmon absorption properties of small Au particles.

The plasmon absorption spectrum of small Au particles changes depending on several physical factors such as the dielectric constants of the material which surrounds Au particles, the size, shape, dielectric constants of small Au particles and dipole–dipole interactions between Au particles [10,18–22]. In the case of the present Au–CuO film, the observed reversibility, wavelength dependent ΔAbs and wavelength shift suggest a possible mechanism in which the change of Au plasmon absorption may be brought about by the change in the dielectric constants of copper oxide upon being exposed to CO, as the redox state of copper oxide can be reversibly changed by exposing to reducing and oxidizing gases in the atmosphere.

The mechanism for selective absorbance increase of the Au–Co_3O_4 composite film by H_2 in the Au plasmon band appears to be complicated and is still not clear. However, the only difference we observed by electron microscopy is that while the average diameter of Au particles was nearly in the same range (10–40 nm) in the Au–Co_3O_4 film, Au–CuO film and Au–NiO film, the size of Co_3O_4 crystallites (5–10 nm) was smaller than the size of CuO and NiO crystallites by a factor of 2–4. This difference in the oxide crystallite size may influence the strength of each factor for the plasmon absorption change of small Au particles, and may lead to the peculiar gas sensing selectivity of the Au–Co_3O_4 composite film.

5. Conclusion

Three types of combined effects of small Au particles on the optical gas sensing characteristics of NiO, CuO and Co_3O_4 films have been compared and discussed.

Small gold particles with diameters of about a few tens nm combined with NiO and Co_3O_4 enhances the catalytic formation of carbonate species on the surface resulting in CO_2 formation in gas phase and thus enhances the CO-sensitive decrease in the light absorption in the whole visible–near IR region. On the other

hand, small gold particles themselves also exhibit gas-sensitive increase in the light absorption at the plasmon absorption region around $\lambda = 600$–700 nm. This phenomenon appeared on CuO for CO and H_2 and on Co_3O_4 for H_2 but not on NiO.

The gas-selective optical change of the Au–Co_3O_4 composite film would be usable for the optical gas sensor which can recognize CO and H_2 in air, probably for the first time among inorganic optochemical sensor materials.

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