A Highly Sensitive Ammonia Gas Sensor Based on an Ag^+/K^+ Composite Ion Doped Glass Optical Waveguide System

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(Received October 12, 1995)

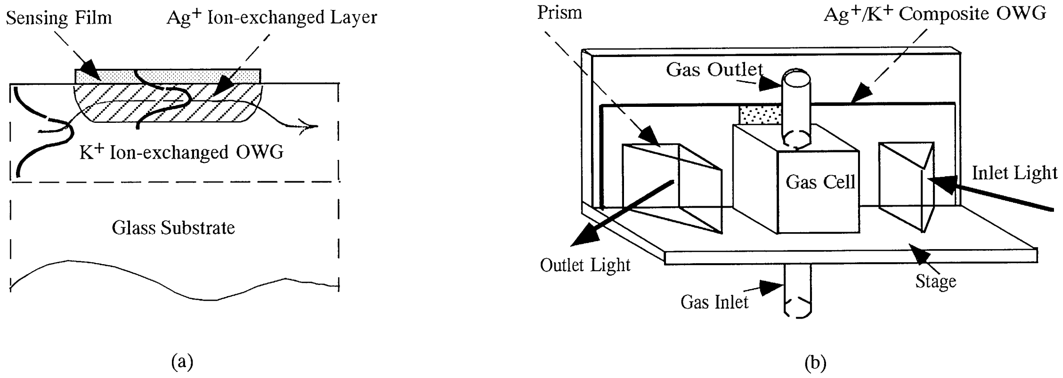
A highly sensitive optical waveguide sensor was developed for gaseous ammonia detection. It was based on an Ag^+ /K^+ composite ion doped glass optical waveguide (OWG). A thin sensing film, consisting of a polymer matrix and a dye, was coated onto the optical waveguide (OWG) surface. Its response was reversible and quick (< 2.5 min), and detection limit was less than 100 ppb.

Ammonia has been known to play an important role in atmospheric chemistry and has been paid great environmental concern. Recently, various kinds of ammonia gas sensors based on different materials have been developed.[1-4] In particular, several sensors fabricated by optical technology have realized very high sensitivities. For instance, an integrated-optic evanescent field ammonia sensor was developed by R. Klein et al. They coated a porous SiO_2 matrix onto a field-assisted ion exchanged optical waveguide (OWG) surface with the sol-gel technique, and a dye was embedded in the SiO_2 layer. With this sensor system, they reported that ammonia gas of 1 ppm was easily detected with the response time of about 300 sec.[4]

However, the essential optical component they used was a multimode optical waveguide (OWG). It is known' that the surface sensitivity of optical waveguide (OWG) depends on the intensity of evanescent field on the OWG surface. Furthermore, a stronger evanescent field can be built-up with a single mode waveguide with high effective refractive index (N_{eff});[5] for example, N_{eff} of single mode Ag^+ ion-exchanged OWGs was about 1.58 and the relative sensitivity (S_{OWG}) of the OWG surface was about 1500 times per unit length of optical path.[6] Such kinds of OWGs, however, have large attenuation of propagating light (α : 5~15 dBcm^{-1}) because of the roughness of the OWG surface,[7] and are difficult to be used for sensor fabrication. To solve this problem, a composite glass ion-exchanged OWG had successfully been developed in our laboratory. It was fabricated by combining a low loss K^+ ion-exchanged OWG (N_{eff} = 1.518, α < 0.5 dBcm^{-1}, S_{OWG} < 100 times/cm) with a highly sensitive Ag^+ ion-exchanged OWG (N_{eff} = 1.58, α : 5 dBcm^{-1}, S_{OWG} ~1500 times/cm) on a glass substrate using tapered velocity coupling as shown in Figure 1 (a). We thus obtained a highly sensitive ion-exchanged OWG with reasonable loss for sensor use.[8] We applied this OWG to construct a highly sensitive ammonia gas sensor.

Figure 1(b) shows the ammonia gas testing system. In order for the system to respond to the ammonia gas, Bromothymol blue was used as an ammonia indicator, and a polymer matrix, cellulose acetate, was used to immobilize the indicator onto the OWG surface. Bromothymol blue, often used as a pH indicator, changes the color from yellow to blue for pH of over 7.6. Figure 2 shows the absorption spectrum of Bromothymol blue in its acidic and basic state. The λ_{max} for the basic form is 624 nm, and hence, a Ne-He laser (wavelength 633 nm) was used as a monitoring light.

The response element in Figure 1(a) was fabricated in the following manner. At first, we prepared the highly sensitive composite ion-exchanged OWG. The glass substrate (size of 76 × 26 mm made of crown glass, "*Shiro Fuchimigaki* (white edge-polished) " purchased from Matsunami Glass Co., Ltd.) was dipped into KNO_3 melt at 400 ℃ for 30 min to obtain a K^+ ion-exchanged OWG layer; and then a piece of frosted glass (10 × 26 mm) covered with a thin layer of $AgNO_3$ mixed with KNO_3 and $NaNO_3$ ($[AgNO_3] : [KNO_3] : [NaNO_3] = 5 : 23.75 : 71.25$ mol%) was fixed onto the surface of the K^+ OWG with a clamp, and the whole sample was heated at 300 ℃ in an electric furnace for 45 min.[8] Second, Cellulose acetate solution (



(a) (b)

Figure 1. (a) the sensitive element of the testing system. (b) the set-up of the testing system. Ne-He laser beam of 633 nm was used as the monitoring light.

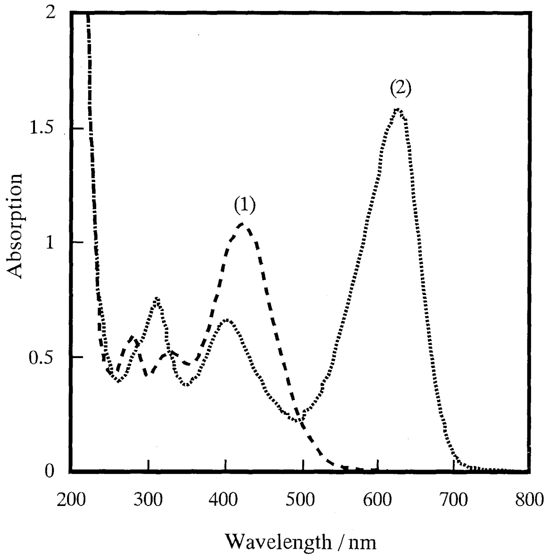


Figure 2. The absorption spectrum of Bromothymol blue in acidic (1) and basic state (2).

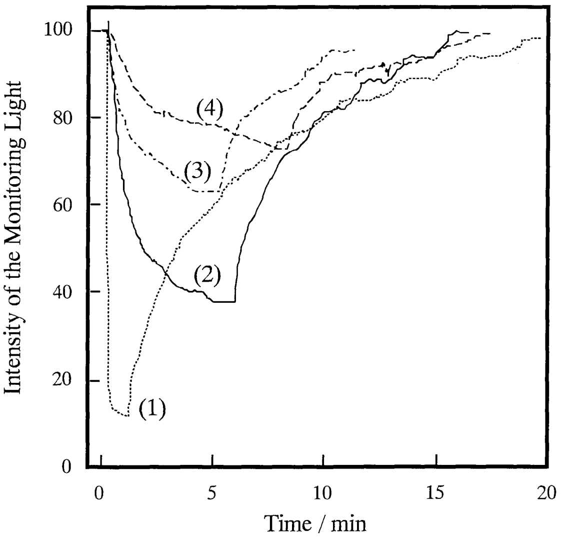


Figure 3. The results of ammonia gas testing. The concentrations of ammonia gas are: (1) 10 ppm, (2) 1 ppm, (3) 200 ppb and (4) 100 ppb.

cellulose acetate : n-butyl acetate : ethanol = 1 : 3 : 1) was mixed with Bromothymol blue (0.1 moldm^{-3}) with 1 : 1 in volume. Third, the mixture was coated in a thin film (ca. 0.1 μm in thickness, and ca. 1.5 in refractive index) onto the surface of the Ag$^+$ ion-exchanged region of the composite OWG by spin-coating as shown in Figure 1(a). In addition, we found that the sensitivity of the indicator for ammonia gas is largely affected by pH of the immobilizing carrier (Bromothymol blue has a pK of 7.0). Thus, sodium hydroxide alcohol solution of 0.002 moldm^{-3}was used to adjust pH of the thin film to enhance the sensitivity of the film against ammonia gas. We prepared several solutions having different pH values, and found out the most appropriate one by trial and error; thus, details of the pH dependence of the sensor are in progress.

The monitoring light in Figure 1(b) was introduced into and out of the OWG with coupler prisms, and a gas cell (20 × 20 × 20 mm) was fixed onto the surface of the polymer film in order to expose the film only to the gas tested. In the flow system, the pre-rarefied ammonia gas of about 10 ppm (v/v) in nitrogen was used as a testing gas, which was diluted further to a definite concentration by using pure nitrogen. Different flow controllers with a maximum flow rate of 2 dm^3 min^{-1} for nitrogen and 0.2 dm^3 min^{-1} for the testing gas were used to obtain a series of concentrations of ammonia gas in the region of 10 ppm to 100 ppb.

The results shown in Figure 3 are the responses of the sensor system for the different concentrations of ammonia gas. The response is reversible, and 100 ppb ammonia gas is easily detected with a response time ($t_{1/e}$) of about 150 sec.

Thus, a highly sensitive ammonia gas sensor has successfully been fabricated by using a highly sensitive OWG with a thin sensing film. This system, however, can be improved in several ways. In particular, the dye used in this system is not particularly selective for ammonia gas, and thus, the other kinds of alkaline gas may interfere. A use of selective membranes, such as metal phosphonate thin films,[9] perhaps will give a better result. However, we can apply the testing system to detect a trace of ammonia in certain cases where the test samples consists of only ammonia and other neutral gases.

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