

Development of ZnO-based surface plasmon resonance gas sensor and analysis of UV irradiation effect on NO₂ desorption from ZnO thin films

Ken WATANABE,[†] Kenji MATSUMOTO, Takeshi OHGAKI, Isao SAKAGUCHI,^{*} Naoki OHASHI,^{*} Shunichi HISHTA and Hajime HANEDA

Sensor Materials Center, National Institute for Materials Science, Namiki 1-1, Tsukuba, Ibaraki 305-0044

*Optical Materials Center, National Institute for Materials Science, Namiki 1-1, Tsukuba, Ibaraki 305-0044

In order to perform a high throughput exploration of sensor materials using surface plasmon resonance (SPR), the gas sensing property of a ZnO/Au/SiO₂ chip with SPR and the enhancing effect of UV irradiation on the desorption rate of NO₂ from the ZnO surface were investigated. When the ZnO/Au/SiO₂ chip was exposed to a high concentration of NO₂ (1000 ppm), a large peak shift was observed in the SPR curve. However, this sensing signal for NO₂ gas did not recover to the baseline. In the case of low-concentration NO₂ (10 ppm), the peak shift of the SPR curve was lower than that in the case of the high-concentration gas, but recovery to the baseline was observed. From the X-ray photoelectron spectra for N 1s of the ZnO thin films exposed to 1000- and 10-ppm NO₂, two chemisorption states—NO₂⁻ (403.7 eV) and NO₃⁻ (407 eV)—were confirmed. After the ZnO film was irradiated by UV rays, exposed to 10-ppm NO₂, all peaks related to N 1s disappeared. However, in the case of the ZnO film exposed to 1000-ppm NO₂, adsorbed NO₃⁻ remained on the surface of ZnO. From these results, it was found that UV irradiation effectively assisted NO₂ desorption from the surface of the ZnO thin film exposed to 10-ppm NO₂.

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1. Introduction

To extend the safety network, advanced sensing against various risk factors is essential. In particular, the development of a high-performance gas sensor is an important step because there are many gas species that are toxic for humans or the environment. Among various types of gas sensors, the semiconductor gas sensor is considered promising. Further, many sensor materials based on metal oxides have been reported.¹⁾

Doping²⁾ or addition³⁾ of other elements in sensor materials is an important design parameter for semiconductor sensors because carrier density and surface morphology strongly affect their sensing properties. However, the exploration of doping or adding materials is a time-consuming process. Therefore, the development of a high throughput exploration of sensor materials is required.

Ion implantation plays an important role in the field of semiconductors, and it has been applied to several materials as a doping and surface modification method because this technique offers high repeatability. Recently, our group has reported a new method of producing a dose library for implantation^{4),5)} and a combinatorial-ion-implantation technique using a mask.^{6),7)} Using these approaches, we can implant an element in a substrate up to concentrations of order of 10¹³ to 10¹⁷ ions/cm². In addition, determining the dose library of implants in the substrate makes it possible to suppress unintentional factors introduced by contamination during annealing. If these approaches can be used for exploration of sensor materials, a high throughput exploration

of sensor materials can be achieved. However, an effective method for the evaluation of the sensing property of a combinatorial-ion-implanted sample has not yet been developed because it is difficult to fabricate a large number of electrodes on such a sample. Hence, we have focused on a surface plasmon resonance (SPR) gas sensor for evaluating the sensing property of a combinatorial-ion-implanted sample.

SPR is one of the useful chemical detection techniques and is generally utilized for bio-chemical measurement applications because it is a very sensitive and direct way of measuring the refractive index of samples. Recently, several researchers have reported an SPR gas sensor using ZnO⁸⁾ or TiO₂.⁹⁾ **Figure 1** illustrates the working principle of an SPR gas sensor. When the SPR sensor is exposed to the target gas, the reaction or adsorption of gas species on the oxide surface occurs. This reaction or adsorption changes the electron density of the oxide. This change in electron density induces a change in the conductance and permittivity of the oxide. As a result, a peak shift of the SPR spectra is observed, and this peak shift can be read as a sensor signal. In addition, it is possible to analyze 2-dimensional SPR spectra.

Hence, in this study, we have aimed to obtain basic data of an SPR gas sensor based on ZnO for the high throughput exploration of sensor materials. The NO₂ sensing property of the SPR gas sensor based on the ZnO thin film fabricated by using the pulsed laser deposition (PLD) technique was investigated. In addition, to investigate the chemisorption states of NO₂ on ZnO and the effect of UV irradiation on NO₂ desorption from the surface of a ZnO thin film, X-ray photoelectron spectroscopy was performed.

[†] Corresponding author: K. Watanabe; E-mail: WATANABE.Ken@nims.go.jp

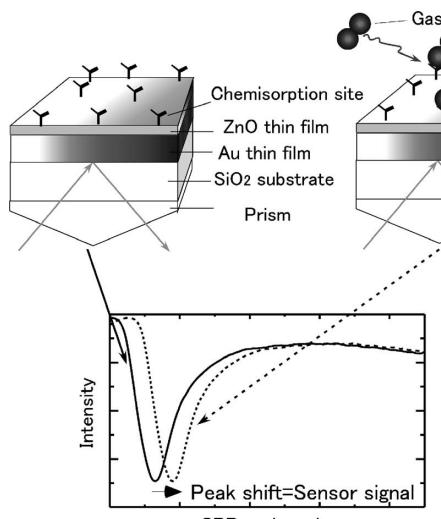


Fig. 1. Schematic representation of an SPR gas sensor.

2. Experimental

In order to utilize the ZnO thin film on Au/glass as SPR sensor chips, silica glass (SiO_2) was used for this optical system because oxide materials are fabricated and heat-treated at a relatively high temperature in various ambient gases.¹⁰⁾ 50-nm-thick Au films were deposited on SiO_2 substrates by using the sputtering technique. ZnO thin films were prepared on the Au/ SiO_2 substrates by PLD as reported elsewhere.¹¹⁾ A polycrystalline ZnO pellet prepared by using a conventional ceramic method was used as the target for PLD. The growth temperature was 200°C, and the total pressure in the vacuum chamber during the deposition was maintained at 1.5×10^{-5} torr by introducing a constant flow of oxygen gas. The fourth harmonic generation (FHG) of pulsed Nd:YAG laser (Quantel, Brilliant B, $\lambda = 266$ nm) was employed and the ZnO targets were irradiated at 5 Hz. The thickness of the prepared ZnO films was 5–7 nm. The surface morphology of these films was observed using the dynamic mode of an atomic force microscope (SPI 400Probe Station, Seiko Instrument Inc.).

A conventional SPR system with Kretschmann configuration (Handy-SPR PS-0109, NTT-AT Corp.) was selected for sensing the vapor-phase species. A 770-nm LED and a CCD line sensor were used as the light source and detector, respectively. For these improvements, the measurement range of resonance curves was fixed to 43°–53°. The gas detection experiments were carried out against the two types of gases, air-diluted NO₂ (10 or 1000 ppm); their flow rate and measurement temperature were 40 ml/min and 24°C, respectively.

X-ray photoelectron spectroscopy was used for the determination of the chemisorption states of NO₂ on the ZnO film. The XPS measurements were carried out using a Sigma probe (VG Scientific, UK) with monochromatic Al $K\alpha$ excitation, and all the binding energies were calibrated to the C 1s peak at 284.8 eV. A high-voltage Hg lamp (EA-250, Hoya Candeo Optronics Corp.) was used as the UV source for the irradiation. The same ZnO/Au/ SiO_2 chip with sensor measurement was used for the XPS measurement. This chip was exposed to 10- or 1000-ppm NO₂ for 5 h in the desiccator. After exposure to NO₂, the XPS measurement was performed, and then UV irradiation for 10 min was carried out under atmospheric conditions.

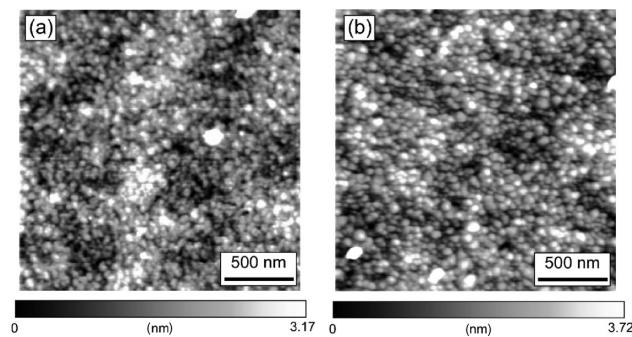


Fig. 2. AFM images of (a) Au/ SiO_2 , (b) ZnO/Au/ SiO_2 .

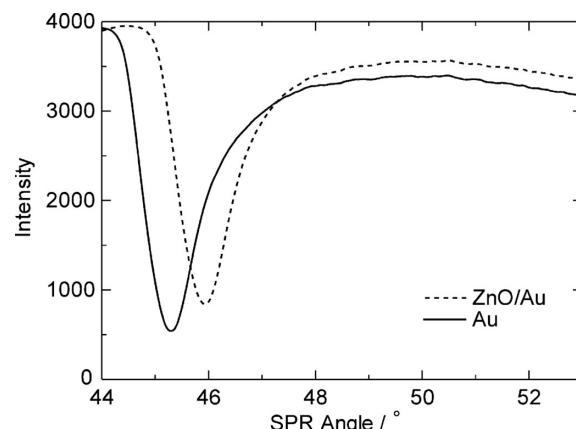


Fig. 3. SPR spectra of (a) Au/ SiO_2 and (b) ZnO/Au/ SiO_2 in air at 24°C.

3. Results and discussion

Figure 2 shows the surface-sectional AFM images of the Au/ SiO_2 and ZnO/Au/ SiO_2 chip. The surface morphology of the ZnO thin film on Au was similar to that of the Au thin film on the SiO_2 substrate because the thickness of the ZnO thin film was 5–7 nm. The grain size of the Au and ZnO/Au thin films was estimated to be approximately 40 and 50 nm from Figs. 2(a) and (b), respectively. These results indicated that ZnO was deposited homogeneously on Au.

To confirm the optical property of Au/ SiO_2 and ZnO/Au/ SiO_2 , the SPR technique has been used. **Figure 3** shows the SPR spectra of the Au/ SiO_2 and ZnO/Au/ SiO_2 chips in dried air at 24°C. As compared to the peak shift of the SPR spectra of the Au film, that of the SPR spectra of the ZnO/Au thin film to a higher angle was observed. This peak shift could be attributed to the change in the dielectric constant upon the formation of the ZnO thin film on Au.

Figure 4 shows the NO₂ sensing property of the ZnO/Au thin film. In the case of the exposure to 1000-ppm NO₂ (Fig. 4(a)), a larger peak shift to a higher angle of the SPR curve was observed as compared to that in the case of the exposure to 10-ppm NO₂ (Fig. 4(b)). However, with respect to the recovery curve, it was found that the peak shift for 1000-ppm NO₂ could not recover to the baseline although the peak shift for 10-ppm NO₂ recovered to the baseline. This result suggests that the chemisorption states of NO₂ on the surface of the ZnO thin film or the reaction between NO₂ and ZnO is dependent of the concentration of NO₂. Furthermore, the recovery time of the peak shift for 10-ppm NO₂ was approximately 200 min. When the SPR measurement is used

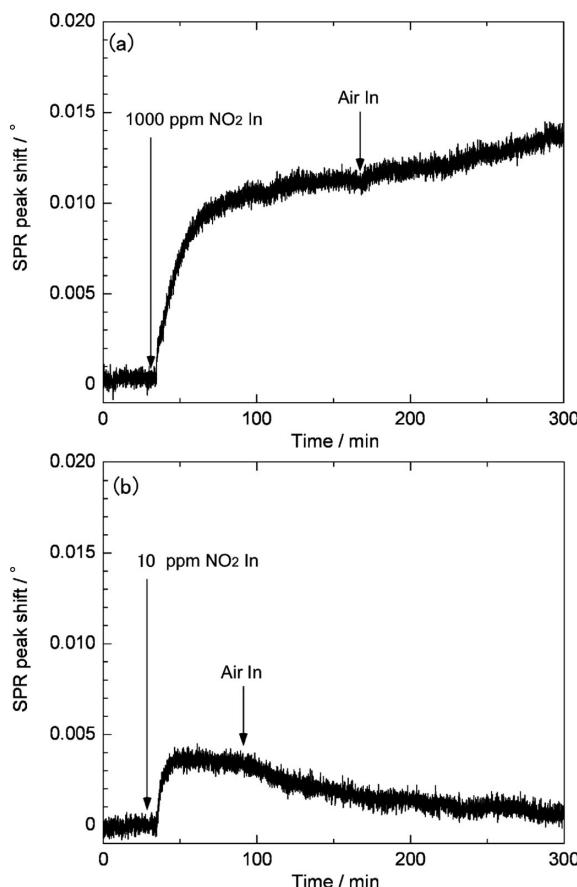


Fig. 4. SPR peak shift of ZnO/Au/SiO₂ in air and (a) 1000- and (b) 10-ppm NO₂.

for material research of a gas sensor, this long recovery time will be a waste of time. Therefore, improvement in the recovery time (NO₂ desorption time) is required.

To reveal the chemisorption state of NO₂ on the surface of ZnO, the XPS measurement was performed. **Figure 5** shows the XPS data collected in the N 1s for a fresh ZnO thin film or ZnO thin films exposed to 10-ppm and 1000-ppm NO₂. As evident from the comparison, the XPS data collected in the N 1s for Zn(NO₃)₂ is also shown in Fig. 5. In the case of the fresh ZnO thin film, no peak related to N 1s was observed. On the other hand, for ZnO thin films exposed to NO₂, mainly two peaks around 407 and 403.7 eV were observed. This implies that there were two chemisorption states of NO₂ on the surface of a ZnO thin film. The peak around 407 eV was assigned to the N 1s transition in the nitrate ion (NO₃⁻) adsorbed on the surface of a ZnO thin film because the highest peak around 407 eV in the XPS spectra of Zn(NO₃)₂ was observed. According to the literature related to the binding energy for NaNO₂,¹²⁾ the peak around 403.7 eV is assigned to the N 1s transition in a nitrite ion (NO₂⁻). Therefore, the peak around 403.7 eV for the samples exposed to NO₂ could be assigned to the N 1s transition in the nitrite ion (NO₂⁻) adsorbed on the surface of the ZnO thin film.

In order to assist the desorption of NO₂ from the surface of the ZnO film, UV irradiation was performed. **Figures 6 and 7** show the XPS data collected in N 1s for the ZnO thin films exposed to 1000- and 10-ppm NO₂, with or without UV irradiation. In the case of the ZnO film exposed to 1000-ppm NO₂, the peak around 407 eV, assigned to the N 1s of the nitrate ion, still remained after

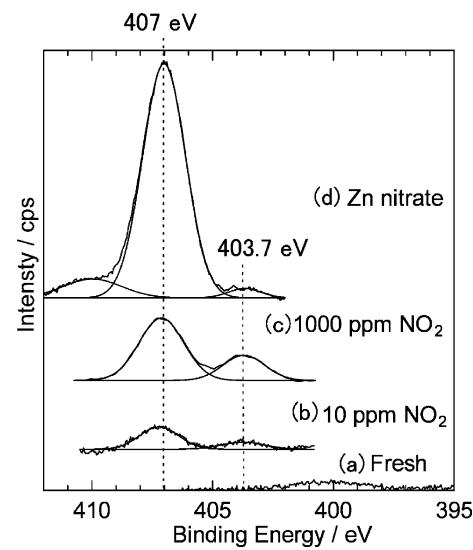


Fig. 5. XPS spectra data collected in N 1s of (a) fresh ZnO and ZnO exposed to (b) 10- and (c) 1000-ppm NO₂. Data for Zn(NO₃)₂ is shown in (d) for the sake of comparison.

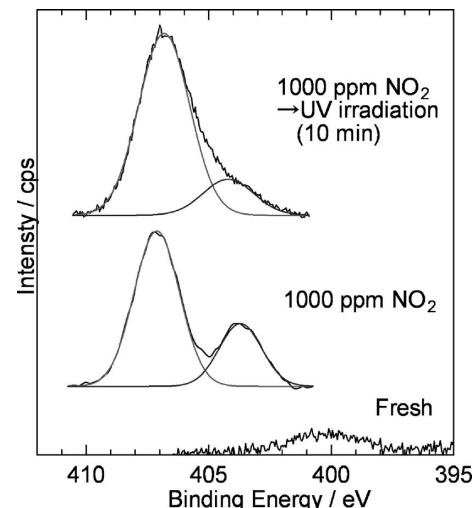


Fig. 6. XPS spectra data collected in N 1s of the ZnO thin film exposed to 1000-ppm NO₂ before and after UV irradiation for 10 min.

the UV irradiation. However, the peak around 403.7 eV, assigned to the N 1s of the nitrite ion disappeared after the UV irradiation. On the other hand, both adsorbed NO₂⁻ and NO₃⁻ were removed from the surface of ZnO exposed to 10-ppm NO₂ after the UV irradiation. In addition, these results show that the desorption of the adsorbed NO₃, whose binding energy was around 407 eV, with UV irradiation seemed to strongly depend on the NO₂ concentration. As mentioned above, the sensor signal could not recover to the baseline in the case of the exposure to 1000-ppm NO₂. On the other hand, in the case of the exposure to 10-ppm NO₂, the sensor signal recovered to the baseline. These results show a good agreement with that of the UV irradiation experiments. Therefore, it seems that adsorbed NO₃⁻ affects the recovery property of ZnO thin films.

With respect to the mechanism for NO₃⁻ formation, the following two models have been reported by Ozensoy et al.¹³⁾ One of these models is the reaction between NO₂ gas and the adsorbed oxygen on the ZnO film as per reaction (1). The other is the

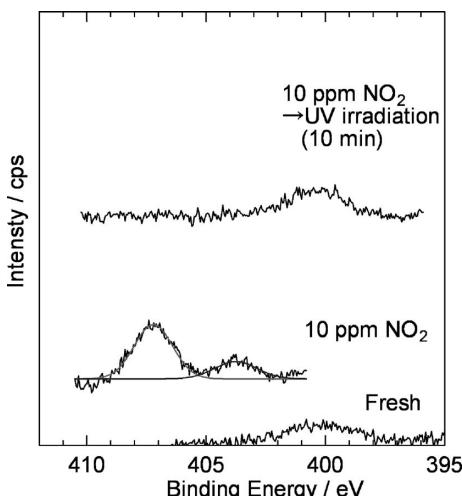
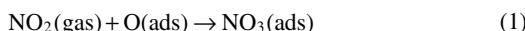


Fig. 7. XPS spectra data collected in N 1s of the ZnO thin film exposed to 10-ppt NO₂ before and after UV irradiation for 10 min.

adsorption of NO₂ on an O²⁻ site of the surface leading to a NO₃⁻-like species as given in reaction (2).



If reaction (2) is noninvertible and a considerable amount of lattice oxygen is consumed by the reaction, the ZnO structure will be destroyed because of the exposure to NO₂ and Zn(NO₃)₂ will be formed on the surface of ZnO. Although this assumption is not evident in the result of this study, it can explain the results of the recovery curve and the UV irradiation effect on the ZnO thin film exposed to 1000-ppt NO₂. Whatever the reason may be, it was found that exposure to a high concentration of NO₂ was not conducive to the high throughput exploration of a sensor material.

In the case of UV irradiation of the ZnO film exposed to 10-ppt NO₂, all adsorbed NO₂ species were removed from the surface of ZnO. This result suggests the possibility of the promotion of the desorption rate of adsorbed NO₂ species from ZnO with a photoinduced hole. From these results, it was found that UV irradiation was effective for the desorption of NO₂ from the ZnO thin film exposed to 10-ppt NO₂. Therefore, UV irradiation for the rapid recovery of a sensing signal can be expected as an application of the high throughput exploration of sensor materials.

4. Conclusion

The NO₂ sensing property of an SPR gas sensor based on a ZnO thin film fabricated by PLD and the UV irradiation effect on the NO₂ desorption from the surface of the ZnO thin film were investigated in order to obtain the basic data for an SPR gas sensor for a high throughput exploration of sensor materials. The fabricated ZnO gas sensor exhibited sensitivity to 10- and 1000-ppt NO₂, and the recover property strongly depended on the concentration of NO₂. From the results of the XPS measurement, two chemisorption states of NO₂ on the ZnO thin film, NO₃⁻ and NO₂⁻, were confirmed. When only the ZnO thin film exposed to 10-ppt NO₂ was UV irradiated, all adsorbed NO₂ species desorbed from ZnO because of a photoinduced hole. From these results, it was concluded that low-concentration NO₂ sensing using SPR and UV irradiation can be expected as an application of the high throughput exploration of sensor materials.

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