Reducing Gas Sensing Based on the Redox Interconversion of Neodymium (III) Chromate(V)

Yoshitaka Aoki,* Hiroki Habazaki, and Hidetaka Konno
Division of Materials Science and Engineering, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628

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The novel sensing property of neodymium (III) chromate(V), $NdCrO_4$, to methanol has been demonstrated. The electrical response of this compound did not rely on the surface potential change by the interaction with methanol gas, but was instead due to the redox interconversion of zircon-type $NdCr^{V}O_4$ to KDP-type $NdH_2Cr^{III}O_4$. The $NdCrO_4$ film prepared on alumina substrates with 2.5-μm thickness could respond to methanol of ppm order concentration with an apparent increase in electrical resistance.

Metal oxide semiconductor gas sensors have been subjected to extensive investigations for industrial and environmental applications because of their excellent features such as low cost, device compatibility, and ease of implementation. Since the pioneering work on the ZnO sensor,[1] many oxides such as WO_3, SnO_2, In_2O_3, TiO_2, and Fe_2O_3 have been studied in the field.[2] However, further development of the novel sensor materials is still in demand because of the widening field of gas sensor applications.

Neodymium (III) chromate(V), $NdCrO_4$, is an unusual pentavalent chromium compound of zircon-type structure (tetragonal, $I4_1/amd$),[3,4] and behaves as a *n*-type semiconductor due to the band-like transport of d^1-electron on Cr^V.[5] Previously, we found that this compound is reduced to *II*-KH_2PO_4-type (KDP-type) $NdH_2Cr^{III}O_4$ in the presence of organic vapor at 543 K, and the reduced phase is restored to the original zircon-type $NdCrO_4$ by air oxidation (Figure 1).[6] The transformation between zircon- and KDP-type phases is not accompanied by the rearrangement of metal atoms. Consequently, a rapid transformation between zircon- and KDP-type phases can be achieved by tilting of the CrO_4 tetrahedra through the redox reaction. Accordingly, it is speculated that the electrical property of $NdCrO_4$ changes in response to the presence of organic vapor, due to the redox interconversion. Here, we report on the methanol gas sensing by the $NdCrO_4$ film sensor.

The $NdCrO_4$ film sensor was prepared on alumina plates by coating with a 1-butanol solution containing equimolar amounts of $Nd(CH_3COO)_3H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$. The solution was applied to the plates ($50 \times 50\,mm^2$) using a brush. Coated plates were dried in air at 353 K for 10 min and annealed at 853 K for 5 min in air. The coating, drying and annealing processes mentioned above were repeated 20 times, and finally the specimens were annealed at 853 K for 1 h in air. The purity of the polycrystalline film samples was checked by means of X-ray diffraction (XRD) analysis. Film morphology was characterized by means of scanning electron microscopy (SEM). The coated alumina plate was cut into rectangular pieces ($20 \times 5\,mm^2$). Two Au pads, $3 \times 5\,mm^2$ spaced 10 mm apart, were deposited on the film of each piece and Au wires were attached to the pads by using Au paste. The electrical response of a $NdCrO_4$ film sensor to methanol vapor was examined by measuring the voltages at an applied dc current of 20 μA, with changing the atmosphere every 10–20 min from air to CH_3OH/air mixed gas, or vice versa. The measurements were performed in a continuous-flow tubular reactor with a quartz tube of 7.0-mm diameter.

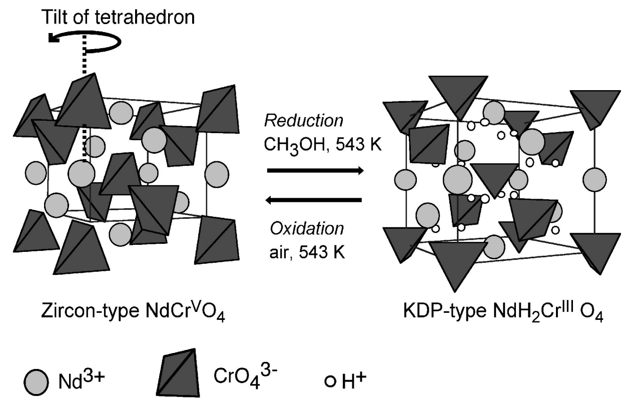

Figure 1. Reversible structure change of the redox interconversion between zircon-type $NdCrO_4$ and KDP-type NdH_2CrO_4 phases. This transformation can be attributed to the tilt of CrO_4 tetrahedron and hydrogen bonding.

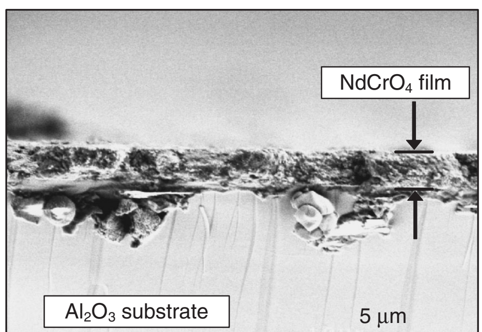

Figure 2. Cross-sectional SEM image of a $NdCrO_4$ film prepared on Al_2O_3 substrate.

Figure 2 shows a cross-sectional SEM image of the as-prepared $NdCrO_4$ film. It is found that a 2.5-μm-thick film is uniformly formed over the alumina substrate. XRD measurement indicates that the film is a single phase of zircon-type, and impurities, such as $NdCrO_3$, Cr_2O_3, and Nd_2O_3, are not formed.

The electrical resistance of the film was in the order of $10^7\,\Omega$ at 293 K, and decreased to the order of $10^5\,\Omega$ with a temperature increase to 523 K in air. This suggests that the $NdCrO_4$ film thus

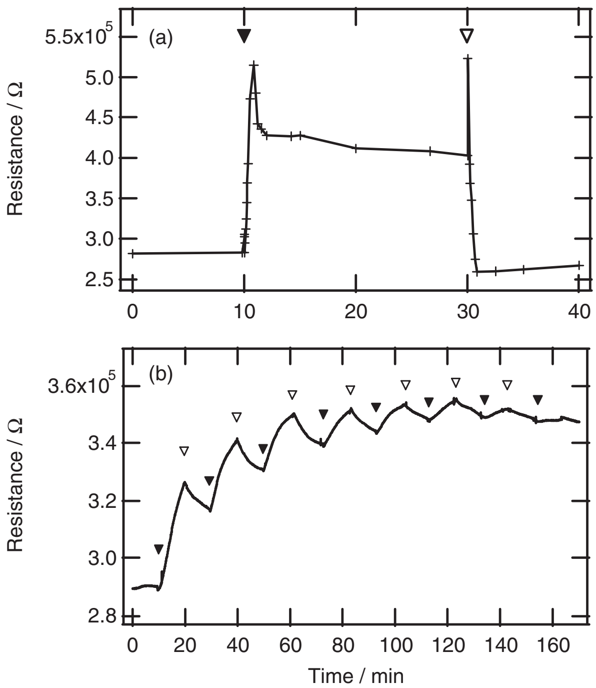

Figure 3. (a) Resistance change of $NdCrO_4$ film upon the switching-on and -off of methanol of 20% in air at 523 K. (b) Response behavior of $NdCrO_4$ film to the switching-on and -off of methanol of 30-ppm concentration every ca. 10 min in inert atmosphere (0.1% O_2) at 523 K. ▼ and ▽ indicate the points of the switching-on and -off of methanol, respectively.

prepared exhibits the semiconducting property. Figure 3a shows the change of electrical resistance of $NdCrO_4$ film at 523 K under the condition of switching-on and -off 20% (v/v) concentration methanol vapor at 523 K in air. The $NdCrO_4$ film exhibits a constant resistance (2.8×10^5 Ω) under the applied dc current of 20 μA at 523 K in air, however, the resistance of the film sharply increases by a factor of 2 upon contact with methanol vapor, and then exponentially decreases and becomes constant at the value which is 1.5 times larger than the resistance value as-maintained in air. In addition, upon the switching-off of methanol, the resistance of the film is rapidly decreased and restored to the value of the resistance of the film as-maintained in air. This electrical response of the $NdCrO_4$ film sensor was retained even after repeating the cycle of switching-on and -off of methanol ten times. Conventional semiconductor gas sensors rely on the change of barrier height of a surface space charge layer through the chemisorption of reducing gas onto the metal oxide surface.[2,7] Hence, *n*-type semiconductor sensors exhibit a decrease of resistance upon exposure to the reducing gases.[2,7] The electrical response of $NdCrO_4$ to the presence of methanol is in contradiction to that of the conventional *n*-type oxide sensors, indicating that it is not dependent on the surface potential change. Therefore, it is clear that the increase of electrical resistance of $NdCrO_4$ film by contact with methanol vapor is due to the reduction of $NdCrO_4$ to NdH_2CrO_4 and the restoration of the resistance by removal of methanol is due to the air oxidation of NdH_2CrO_4 to $NdCrO_4$. The XRD pattern of $NdCrO_4$ film exposed to 20% methanol vapor at 523 K for 30 min in air was almost the same as that of a zircon-type phase, suggesting that most of the zircon-type $NdCrO_4$ in a film remains after 30 min reduction. The results of the sensing and XRD experiments indicate that the $NdCrO_4$ film exhibits the increase of electrical resistance by a factor of 2 by the reduction of only a part of the bulk.

We carried out sensing experiments with low-concentration methanol vapor. However, the $NdCrO_4$ film sensor did not respond to methanol vapor at less than 3% concentration in air. We examined the response of $NdCrO_4$ film to the vapor concentrated in ppm order under an inert atmosphere. Figure 3b shows a response curve to the switching-on and -off of 30-ppm methanol vapor several times in Ar at 523 K. It was found that the resistance of the $NdCrO_4$ film sensor was increased by the reaction with the 30-ppm concentration methanol vapor at 523 K, although the rate of this increase was much slower than that occurring upon contact with the high-concentration methanol. As the standard Ar gas used in this study contains about 0.1% oxygen (v/v), the $NdCrO_4$ film can be re-oxidized by the switching-off of the methanol. However, the restoration rate of electrical resistance by oxidation was much slower than that occurring in air, and the resistance was not restored completely by oxidation in an inert atmosphere for 10 min. After repeating the cycle of switching-on and -off of methanol seven times, the $NdCrO_4$ film sensor responded only negligibly to the dilute methanol gas. The deterioration of the responce may be attributed to the difficulty in restoration from Cr^{III} to Cr^{V} under low oxygen partial pressure.

Herein, we have demonstrated that $NdCrO_4$ sensitively changes its electrical resistance in response to the presence of methanol vapor. The electrical response is due to the redox interconversion reaction of $NdCrO_4$, and is not related to the surface interaction. Without optimization, a $NdCrO_4$ film of 2.5-μm thickness can respond to 20% concentration methanol vapor at 523 K in air and also to the vapor of ppm order in an inert atmosphere (0.1% O_2). Therefore, it can be concluded that the $NdCrO_4$ film offers the potential for providing a novel reducing-gas sensor material. In future, we will report on the sensing properties under ambient atmosphere.

References and Notes

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