Preparation of Cr-Doped TiO_2 Thin Film of P-type Conduction for Gas Sensor Application

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Titanium dioxide (TiO_2) could be doped with as much as 8.7 atom% Cr by means of a sol-gel method. XRD analysis revealed that the powder of Cr (8.7 atom%)-doped TiO_2 calcined at 500 °C consisted of small crystallites ascribale to anatase structure. The thin film of doped TiO_2 ($70\,\mu m$) at this composition was found to behave as a p-type semiconductor on exposure to CO and NO_2 in air: it responded to dilute NO_2 with a sharp decrease in electrical resistance.

Semiconductor gas sensors have been subjected to extensive investigations for practical applications owing to their excellent features such as low cost, good performance and easy implementation. Among the semiconducting metal oxides used or tested so far, TiO_2 exhibits probably the best chemical stability to high temperatures and harsh atmospheres. This feature makes the oxide suitable for high temperature applications, and in fact a bulk-type oxygen sensor, which changes its electrical resistance through a nonstoichiometric change of bulk TiO_2, has been commercialized in a massive scale for the air/fuel ratio control of car engines. Titanium dioxide itself is an n-type semiconductor, but its conductivity is usually too poor to permit a surface type sensor which changes its resistance through the interaction of TiO_2 surface with gases, although a CO sensor using the anatase phase of TiO_2 has been reported.[1] This difficulty increases even more in the case of detecting oxidative gases, the adsorption of which usually causes the resistance of a n-type sensor to increase.[2] Upon exposure to NO_2, for example, the electrical resistance of TiO_2-based devices often go beyond the measurement limit of conventional circuitry. It has been attempted to decrease the resistance of TiO_2 based thick films by doping with a pentavalent metal (Nb).[3,4] It is considered, however, that a better solution may come out if the electronic structure of TiO_2 can be altered into p-type. From this expectation, we tried to modify TiO_2 by heavy doping with Cr (trivalent). It was found that the doping brought forth a thin film of p-type conduction which could respond to dilute NO_2 with a sharp decrease in resistance, as described below.

Sols of undoped and Cr-doped TiO_2 were prepared, as follows. For the undoped TiO_2, a solution (0.5 M) of titanium isopropoxide in isopropanol solvent was added dropwise to an acidic water containing HNO_3 under stirring. The amounts of water and HNO_3 were set to satisfy $[H_2O] : [HNO_3] : [Ti] = 112 : 1 : 1$ in molar ratio at the final stage of reaction. This gave a transparent yellow sol of TiO_2. For the Cr-doped samples, chromium acetate, suspended in 2-methoxyethanol, was added to the starting titanium isopropoxide solution by an amount of 2 or 10% in Cr/Cr + Ti atomic ratio. By following the same procedure as above, green colored sols were obtained. Each of these sols was gellified by slowly increasing the pH up to about 3 with the addition of an aqueous solution (1 M) of NH_4HCO_3, and then centrifuged to collect a gel. Part of the gel was dried at 80 °C and by X-ray fluorescence spectrometry (TXRF) the Cr contents were found to be 1.8 and 8.7 atom% for the low and high doped samples, respectively. Each of the wet gels obtained above could be ultrasonically dispersed in water to form a colloidal suspension free of precipitates when the content of colloidal particles was set to be about 3 mass%. The colloidal suspension was spin-coated onto an alumina substrate with printed gold electrodes and the resulting film was calcined at 600 °C for 3 h. Gas sensing behavior of each film was tested in a gas-flow apparatus equipped with heating facilities. The electrical resistance of each film was measured while the flowing gas was switched between synthetic air and sample gases of CO or NO_2 diluted in synthetic air.

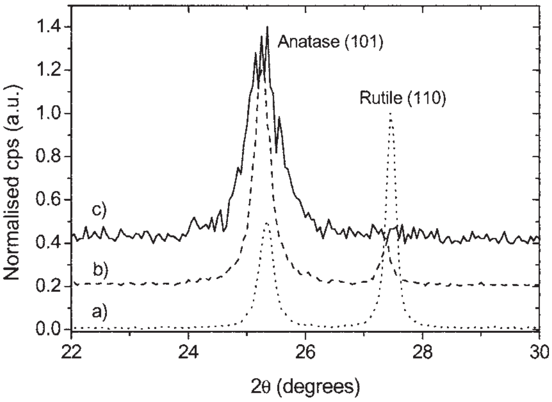

Figure 1. XRD patterns of powder samples calcined at 600 °C; a) TiO_2 (undoped); b) Cr (1.8 atom%)-TiO_2; c) Cr (8.7 atom%)-TiO_2.

It is known that TiO_2 crystallizes in three different phases of brookite, anatase and rutile, among which the last is thermodynamically stable at high temperature. As seen from the XRD patterns in Figure 1, the undoped sample after calcination at 600 °C was a mixture of anatase and rutile phases. For the Cr-doped TiO_2, on the other hand, the anatese dominated over the rutile in the low doped sample and became exclusive in the high doped one. No reflections ascribable to chromium oxides could be observed even for the high doped sample calcined at 1000 °C. Evidently the anatase phase was thus stabilized with the Cr-doping. In addition, the diffraction peak of anatase (101) became broader as the Cr content increased. As estimated from the full width of half maximum intensity of this diffraction peak, the crystallite size was 26, 19 or 13 nm for the undoped, low doped or high doped sample, respectively, indicating that the Cr doping hinders the crystal growth of TiO_2. The ionic radius of Cr^{3+} (61.5 pm, octahedral coordination) is very close to that of Ti^{4+} (60.5 pm, octahedral). This seems to facilitate the Cr doping into the bulk of TiO_2. The diffraction peaks of anatase (101) and rutile (110) shifted to the lower 2θ side on going from the undoped TiO_2 to the Cr (1.8 atom%)-doped, indicating a slight expansion of the

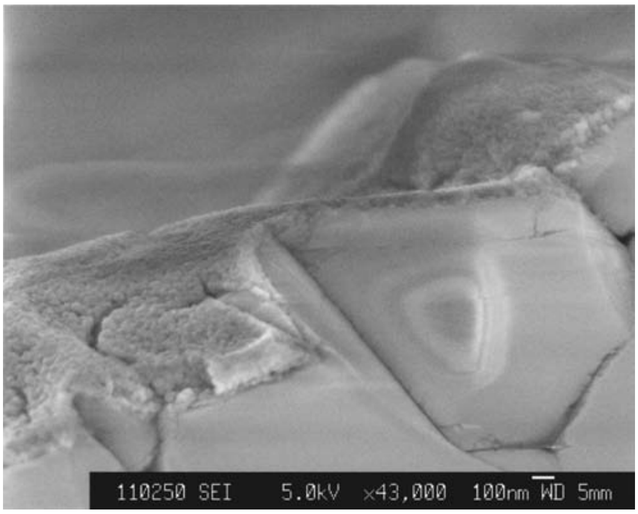

Figure 2. FE-SEM image of Cr (8.7 atom%)-TiO$_2$ thin film with Cr doped on an alumina substrate (cross sectional view).

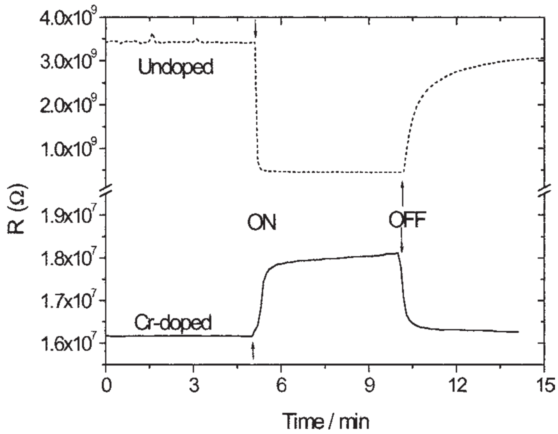

Figure 3. Response transients of undoped and Cr (8.7 atom%)-doped TiO$_2$ films to switching-on and -off CO (1000 ppm) in air at 500 °C.

unit cell. However, no further shift of anatase (101) was visible for the Cr (8.7 atom%)-doped TiO$_2$ and further studies are needed to conclude the state of doped Cr^{3+} ions.

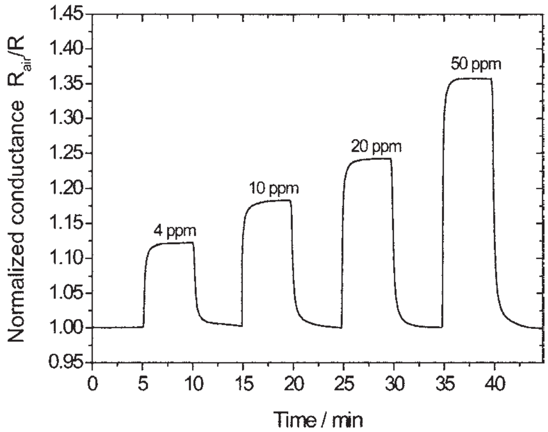

Figure 4. Response transients of Cr (8.7 atom%)-TiO$_2$ film to switching-on and -off various concentrating of NO$_2$ in air at 500 °C.

Figure 2 shows an FE-SEM picture (crosssectional view) of the high doped film (Cr 8.7 atom%). A layer of Cr-TiO$_2$ about 70 nm thick is seen to cover well the surface of gross particles of alumina. Figure 3 shows the response transients of the undoped and Cr (8.7 atom%)-doped TiO$_2$ films to switching-on and -off 1000 ppm CO in air at 500 °C. For the undoped film, the electrical resistance in air (R_{air}, base line) was very large (3.5×10^9 Ω) and decreased almost stepwise on exposure to CO. This change is quite natural for an n-type oxide because CO deprives adsorbed (or surface) oxygen of TiO$_2$. For another film, on the other hand, the resistance increased on exposure to CO, indicating the p-type nature of the film. Moreover, the base line resistance (1.62×10^7 Ω) was smaller than that of the undoped film by almost 2 orders of magnitude. In view of the p-type nature and the reduced resistance, this particular film was expected to respond well to NO$_2$ in air. This expectation turned out to be the case, as illustrated in Figure 4, where the response transients to NO$_2$ (4–50 ppm in air) at 500 °C are depicted in terms of the normalized conductance. The resistance decreased on contacting with NO$_2$, in accordance with the p-type character of the film. The response transients were sharp and stable even at the smallest concentration of NO$_2$ examined (4 ppm). Although the sensitivity defined as R_{air}/R remained rather modest, high stability of the base line and the response transient (low noise and low drift) appears to compensate it. The same test was carried out at other temperatures. The sensitivity increased significantly at 400 °C, but this was at the cost of increasing R_{air} to a too high value (ca. 10^8 Ω). The sensitivity decreased at 600 °C owing mainly to the increase of the decomposition of NO$_2$ to NO. No such responses to NO$_2$ was obtained with the undoped and Cr (1.8 atom%) doped films because of the too high resistances. It is expected that the Cr^{3+} ions incorporated in the lattice points of Ti^{4+} ions act as electron acceptors. Although n-type nature of TiO$_2$ will remain when the Cr content is small, it would be possible that p-type nature is induced when the Cr content is large enough. It is considered that the Cr (8.7 atom%)-doped film was brought to p-type in this way, but the optimum doping condition is yet to be established.

As mentioned above, Cr-doped TiO$_2$ thin films containing Cr as much as 8.7 atom% was successfully prepared by using a sol-gel method and spin-coating technique. Unlike the undoped TiO$_2$ film (n-type), the Cr (8.7 atom%)-doped one showed p-type character and responded well to dilute NO$_2$ in air by a sharp decrease in electrical resistance. This seems to show the importance of such heavy doping in the research of electronic materials, though further studies are needed to elucidate the doping state and the optimum dopant content.

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