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Room temperature ozone sensing properties of p-type transparent oxide $CuCrO_2$

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ABSTRACT

The sintered bulk $CuCrO_2$ and thin film were prepared by sol–gel and pulsed laser deposition, respectively. They show rhombohedral 3R structure, wide band gap and p-type semiconducting properties. These properties are similar with those of $CuAlO_2$, which has been found to be a promising candidate for inexpensive p-type and transparent ozone sensor. In this study, the room temperature ozone sensing properties of the sintered bulk $CuCrO_2$ and thin film were investigated. Furthermore, transparent p-type semiconductor $CuCrO_2$ shows selective and reversible response to ozone at room temperature. This study suggests that $CuCrO_2$ can be another promising candidate for parent materials of room temperature ozone sensor besides $CuAlO_2$.

1. Introduction

Ozone is a strong oxidizer and is widely used for purification, deodorizing, and sterilization applications in pharmaceutical, food, textile, and water supply. However, long time exposure to high concentration of ozone is very harmful to human health. Therefore, it is important to monitor ozone gas.

A number of conventional analytical methods are available for accurate analysis of ozone concentrations in air. However, these standard methods often require sophisticated air sampling and expensive analytical equipment. Semiconductor sensors, such as the sensors based on WO_3 and In_2O_3, are the most economical sensors, but they have a general drawback that they require operation at high temperatures of more than 150 °C [1,2]. Furthermore, the response reversibility of the sensor at high ozone concentration is often poor because of the strong oxidizing property of ozone [3]. Though room temperature sensing of ozone has been achieved in In_2O_3 and ZnO by the activation of the UV light, the usage of UV light limits its application in simple, low-cost and compact sensors [4,5]. It is, therefore, challenging to produce sensors that exhibit high sensing properties at room temperature (RT).

Delafossites $CuMO_2$ (M is trivalent cation, such as Al, Cr and Sc), as p-type transparent conducting oxides (p-TCOs), have gained intense interests due to their potential application in 'invisible circuits', diluted magnetic semiconductors and thermoelectric materials [6–8]. Their structure can be described as sheets of edge-shared MO_6 octahedra alternating stacked with close-packed Cu-ions layers. Delafossites $CuMO_2$ can form either rhombohedral 3R ($R\bar{3}m$) or hexagonal 2H ($P6_3/mmc$) structures, depending on the stacking of the layers [9]. Zheng et al. has reported in 2004 that $CuAlO_2$ shows selective and reversible response to ozone gas at room temperature, which demonstrated the feasibility of developing a low-cost RT ozone sensor [10]. In their research, the response of the sintered bulk $CuAlO_2$ and thin films to 1000 ppm ozone gas has been investigated. However, to our knowledge, there have been no reports on the ozone sensing properties of $CuCrO_2$. Since $CuCrO_2$ shows similar structural and electrical properties with $CuAlO_2$, we predict that $CuCrO_2$ may be another promising candidate for RT ozone sensor.

In this article, the structural, optical and electrical properties of the sintered bulk $CuCrO_2$ and thin film were investigated, and RT ozone sensing properties were studied.

2. Experimental procedure

Sintered bulk $CuCrO_2$ was synthesized by sol–gel method [11–13]. Firstly, stoichiometric $Cu(CH_3COO)_2{\cdot}H_2O$ (99%) and $Cr(NO_3)_3{\cdot}9H_2O$ (99%) were dissolved in distilled water with the addition of appropriate citric acid. The mixtures were stirred for several hours in order to get a well-mixed solution. Then the solution was dried at 373 K and 673 K for several hours to expel the organics. The obtained powder was sintered for 10 h at 1273 K in air, and then was ground and pressed into pellets. Finally, the pellets were sintered at 1273 K for 10 h in air.

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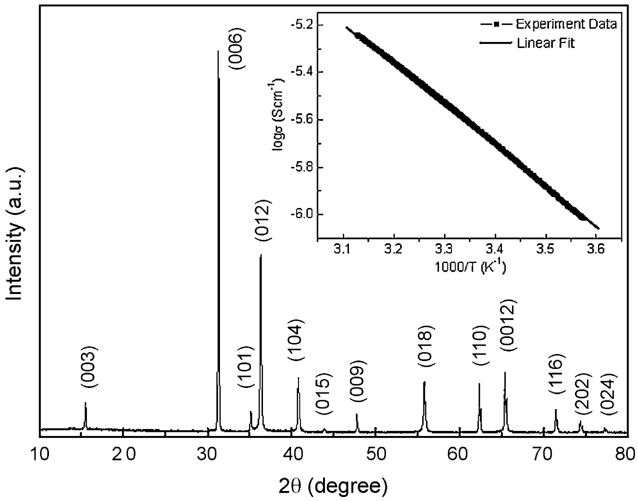

Fig. 1. XRD pattern of the sintered bulk $CuCrO_2$. Inset is the temperature dependence of conductivity for the sintered bulk $CuCrO_2$.

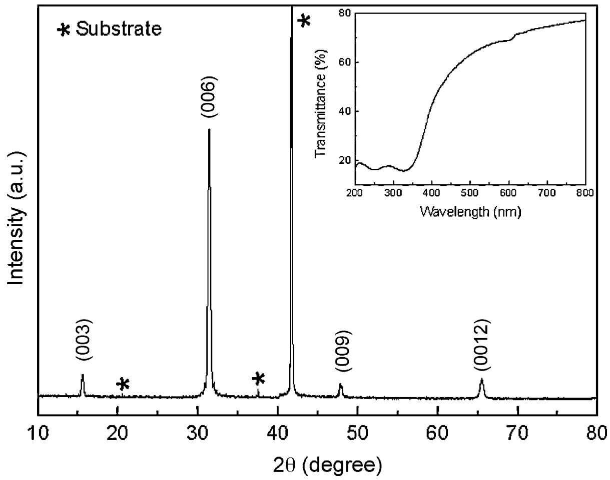

Fig. 2. XRD pattern of the $CuCrO_2$ thin film. Inset is the optical transparency of the film.

$CuCrO_2$ thin films were deposited on (0 0 l) sapphire substrates by pulsed laser deposition (PLD) using the sintered bulk $CuCrO_2$ as target. A pulsed KrF laser with 243 nm wavelength and 5 Hz repetition was used in our experiments; the pulse energy was 100–120 mJ. The pressure of the deposition chamber was about 1×10^{-6} Pa, the temperature of the substrate was kept at 800 K, and the deposition time was 30 min.

A Philips X'pert PRO X-ray diffractometer (XRD) with Cu Kα source was used to identify the crystalline phases. An atomic force microscope (AFM) was used to check the surface morphologies and roughness of the $CuCrO_2$ films. The temperature dependence of the conductivity was measured by the standard four-probe method by means of the cryogenic refrigeration equipment. An optical transmission spectrum of the thin film was measured at room temperature by a dual beam spectrophotometer (VARIAN designed CARY-5E). The ozone gas response of the specimen was measured at room temperature. The ozone source is a commercial ozone calibrator OPSIS OC500 which can generate ozone gas in a range of 20–1000 ppm using compressed dry air. A computer-assisted system recorded the electrical resistance response of the sample.

3. Results and discussion

Fig. 1 shows the XRD result of the sintered bulk $CuCrO_2$. It can be seen that all diffraction peaks can be ascribed to delafossite-structured 3R-$CuCrO_2$ phase (JCPDF No. 89-6744) without any trace of undesired materials. The temperature dependence of conductivity for the sample is shown in the inset of Fig. 1. In the measured temperature range, the conductivity is thermally activated through room temperature with the activation energy E_A about 0.34 eV.

Fig. 2 shows the XRD result of $CuCrO_2$ thin film. Highly (0 0 l) textured single 3R-$CuCrO_2$ phase with no trace of impurity phase can be observed. The optical transmission spectrum of the thin film in visible region is shown in the inset of Fig. 2. The average transmittance of the thin film in the visible region is ∼70%. The direct optical band gap is evaluated to be 3.15 eV.

Fig. 3 shows the selectivity and reversible sensing to 100 ppm ozone of the sintered bulk $CuCrO_2$ and thin film at 300 K. The sensitivity was obtained by $R_{\mathrm{ozone}}/R_{\mathrm{air}}$. The resistivity response of the $CuCrO_2$ thin film to O_2–Air–O_2 circles is studied as shown in Fig. 3(a). No obvious resistivity change is found. It can be seen in Fig. 3(b) and (c) that the thin film and the sintered bulk sample show quick initial responses to the introduction and cutting off of ozone. Since $CuCrO_2$ is a p-type semiconductor, the ozone absorption results in an enhanced concentration of holes near the surface. Therefore, the resistivity of the samples decreases after the introduction of ozone and recovers when ozone is cut off. The response time of $CuCrO_2$ thin film is about 4 min to 90% of the final value and the recovery time is about 2 min to 10% of the steady state signal.

The thin film prepared by PLD is relatively smooth and dense, as shown in Fig. 4. The root mean square (RMS) roughness is determined as 1.8 nm over the 2 μm × 2 μm range for the film. The sensitivity of the $CuCrO_2$ thin film is relatively lower than that of $CuAlO_2$ reported by Zheng et al. In their research, $CuAlO_2$ films were synthesized by metalorganic decomposition (MOD) process. Films prepared by MOD method are often porous because during the sintering process the carbons and organics are expelled from the films and then holes formed [14]. It is generally believed that porous materials has relatively large specific surface areas, and the larger the area is, the higher the adsorption becomes, which results in higher sensitivity [3].

Though the sensitivity is not yet sufficiently high for practical use, $CuCrO_2$ can be a candidate for parent compounds. The sensitivity of a parent compound is typically low for semiconductor sensors. Finding a basic compound that can respond to ozone at RT is important, since low sensitivity can be improved greatly by the addition of impurities. The dense and smooth surface, which is one of the advantages of PLD for thin film preparation, may be a reason for the low sensitivity of $CuCrO_2$ thin film. Therefore, porous nanocrystalline thin films prepared by sol–gel may have enhanced sensitivity.

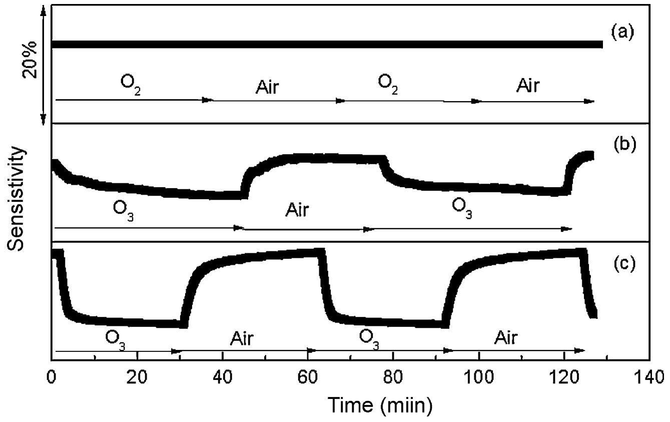

Fig. 3. The response of $CuCrO_2$ thin film (a) to O_2–Air–O_2 circles at 300 K; the response of $CuCrO_2$ thin film (b) and sintered bulk (c) to 100 ppm ozone–Air–100 ppm ozone at 300 K.

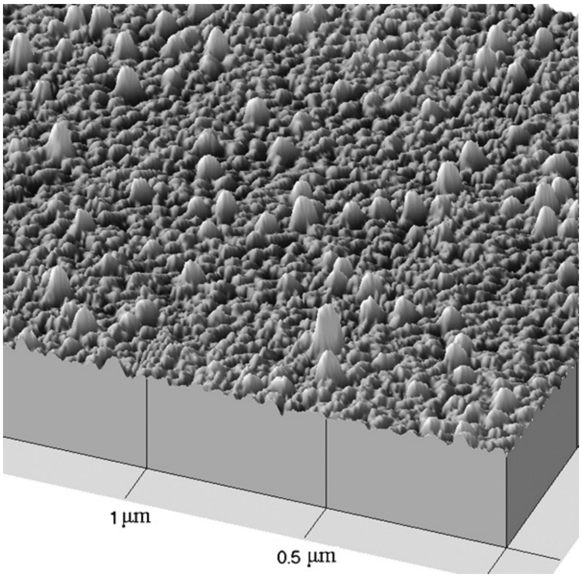

Fig. 4. AFM image of the $CuCrO_2$ thin film.

4. Conclusion

In summary, sintered bulk $CuCrO_2$ and thin films were prepared by sol–gel method and PLD, respectively. The structural, optical and electrical properties were studied. The results show that $CuCrO_2$ is a p-type transparent semiconductor. Furthermore, selective and reversible responds to ozone for both sintered bulk $CuCrO_2$ and thin films have been found at RT, suggests that the p-type transparent $CuCrO_2$ can serve as RT sensor for ozone.

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