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Defect and electrical properties of nanocrystalline tungsten trioxide*

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Nanocrystalline tungsten trioxide particles were prepared by a wet-chemical method. Transmission electron microscope (TEM) analysis shows that the average grain size is about 15nm. The oxygen deficiency of nanometre-sized sample is higher than that of ordinary tungsten trioxide. The electric conductivity increases because of high oxygen deficiency. Ironic relaxation polarization and crystallographic shear (CS) planes theory were used to explain the unusual dielectric characteristic of nanocrystalline tungsten trioxide.

Keywords: nanocrystalline, tungsten trioxide, electrical properties
PACC: 6146, 7280, 7700

1. Introduction

Tungsten trioxide (WO_3) has received much attention because of its potential for many technological applications, such as electrochromic devices, gas sensors and varistors.[1−3] Many studies have shown that some properties of crystalline tungsten trioxide are closely related to grain boundaries. Nanocrystalline tungsten trioxide should show characteristics different from the ordinary material because of its enormous number of grain boundaries.[4] As for nanocrystalline tungsten trioxide, more attention was concerned with thin films.[2] Researches about nanometre-sized bulk tungsten trioxide are quite few, especially for its electrical properties.

The defect-free WO_3 single crystals are transparent with a band gap of about 2.9eV at room temperature. However, commercial WO_3 powders have yellow or yellow-greenish colour and appear to be n-type semiconductor due to the presence of bulk defects, labelled as WO_{3-y}.[5] Many studies have shown that electrical properties of tungsten trioxide depend strongly on oxygen deficiency, i.e. the value of y.[6,7] Therefore, it is important to know the value of y. Oxygen deficiency y has been measured in this work by using a chemical method.

There are several methods to prepare nanometre-sized tungsten trioxide particles, such as emulsion method, sol-gel technique.[8] In this work, nanocrystalline tungsten trioxide particles are prepared by a new wet-chemical method. Compared with others, this method is simple, feasible and economical. To characterize the nanocrystalline tungsten trioxide, its microstructure and electrical properties are studied.

2. Experiment

Nanocrystalline tungsten trioxide particles were prepared by a wet chemical method. A certain amount of ammonium tungstate ($(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$) powders were dissolved in distilled water to form transparent colloid solution of $WO_3\cdot 2H_2O$. Then diluted hydrochloric acid (10%) was added drop by drop with stirring till pH value became 2. Some precipitate was obtained after the solution was left aging in a water-bath crucible for about four days at 40°C. After being dried, the precipitate was calcined in a muffle furnace for 30min at 450°C to form nanocrystalline tungsten trioxide particles.

A transmission electron microscope (TEM, HITACHI X-600, Japan) was used to observe the size and

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shape of the particles. For composition characterization, the samples were analyzed by using an electron probe microanalyzer (EPMA, JXA-8800R, Japan). X-ray diffraction (XRD) experiments were performed with a Rigaku x-ray diffractometer (D/MAX-3C, Japan) with CuKα radiation of 0.154nm in wavelength. Oxygen deficiency was determined by a chemical method developed by Tan *et al*[9] with the relative error <0.1%. In addition, oxygen deficiency could be obtained by EPMA analysis. As this method is not very accurate, we use it only for comparison.

For electrical measurement, the powders were pressed into pellets of 16mm in diameter at a pressure of 20MPa. Liquid In–Ga alloy contacts were used as electrodes. Current–voltage characteristics were measured by using a stabilized dc supply (WYK3002) and a data acquisition/switch unit (Agilent 34970A) controlled by an automatic measuring system. The dielectric properties were investigated with a precision LCR meter (HP 4284A).

For comparison, a micron-sized sample (μm-WO_3) was prepared by using commercial WO_3 powders and its electrical properties were measured.

3. Results and discussion

The TEM micrograph of nanoparticles prepared by the wet-chemical method is presented in Fig.1. It can be seen that the particles are basically spherical in shape with some agglomeration. The average grain size d is about 15nm.

EPMA analysis reveals only the existence of O and W atoms with the ratio of about 1.84 for nanometre-sized sample. Thus, the oxygen deficiency y equals 1.16. As for micron sample, the ratio of O and W is 2.72, i.e. y equals 0.28.



Fig.1. TEM micrograph of nanometre tungsten trioxide particles.

The oxygen deficiency y of nanometre samples measured by chemical method is 0.93. As for micron sample, y is 0.21. It can be seen that the value of y obtained from chemical method is in accord with that from EPMA analysis. Oxygen deficiency of nanometre sample is higher than that of micron sample.

Figure 2 shows the XRD pattern of nanometre sample prepared by wet-chemical method. The diffraction peaks were obviously broadened, as compared with those of micron sample. The mean grain size d is 12nm, which is a little less than the value obtained from TEM analysis, according to x-ray diffraction line broadening method.[10] XRD analysis of nanometre sample reveals the existence of monoclinic phase of WO_3 (γ-WO_3).

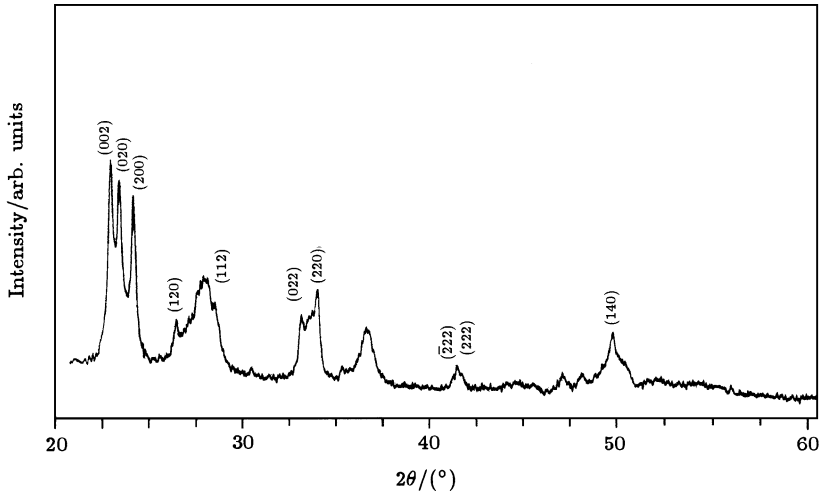


Fig.2. XRD pattern of nanocrystalline tungsten trioxide.

The current–voltage (I–V) characteristics of the samples are shown in Fig.3. It can be seen that the I–V curve of nanometre sized WO_3 (nm-WO_3) is asymmetric with weakly nonlinear behaviour in the positive voltage region and linear behaviour in the negative region, while the experimental fact that the I–V behaviour of μm-WO_3 is comparatively symmetric indicates that there is an additional polarization mechanism in nm-WO_3.[11]

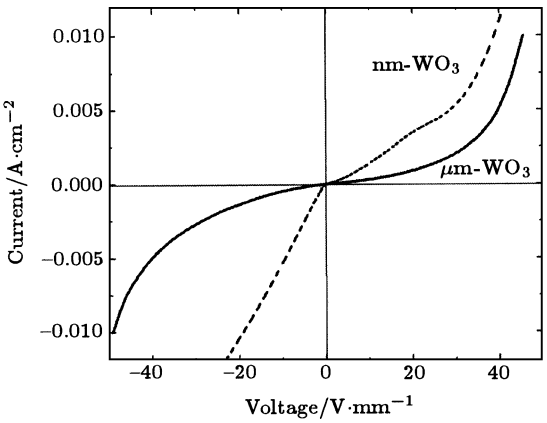


Fig.3. I–V characteristics of nm-WO_3 and μm-WO_3.

The nonlinear coefficient is determined by using the formula

$$\alpha = \frac{\lg(I_2/I_1)}{\lg(U_2/U_1)}, \qquad (1)$$

where U_2 is the voltage corresponding to I_2= 10mA/cm^2, and U_1 corresponding to I_1=1mA/cm^2. The electric conductivity σ in the ohmic region was calculated at a low electric field of 1V/mm. The nonlinear coefficient and electric conductivity in the positive and negative voltage regions (α_+, α_-, σ_+, σ_-) are shown in Table 1. The electric conductivity is obviously different in the two voltage regions for nm-WO_3, which may be attributed to the effect of polarization. The electric conductivity of nm-WO_3 is higher than that of μm-WO_3, both in positive and in negative voltage regions. It is believed that large numbers of carriers are introduced in nm-WO_3 because of its high oxygen deficiency which leads to the high electric conductivity.

Table 1. The nonlinear coefficient and electrical conductivity in positive and negative voltage regions for different samples.

	α_+	α_-	$\sigma_+/(\times10^{-6}\mathrm{S\cdot cm^{-1}})$	$\sigma_-/(\times10^{-6}\mathrm{S\cdot cm^{-1}})$
nm-WO_3	1.45	1.05	7.4	50
μm-WO_3	3.03	2.12	2.5	4.2

The dielectric spectra are shown in Fig.4 (permittivity ε versus frequency f) and Fig.5 (dielectric loss tgδ versus frequency f). The permittivity of nm-WO_3 and μm-WO_3 was found to decrease sharply with increasing frequency, while ε of nm-WO_3 is much higher than that of μm-WO_3 at low frequency. The dielectric loss tgδ of nm-WO_3 increases with increasing frequency, reaches a maximum at f=120Hz, then decreases with further increase of frequency. However, no peak exists in the spectrum of tgδ versus f of μm-WO_3. Many nanostructured materials exhibit ultrahigh permittivity, which is supposed to arise mainly from interfacial polarization, rotation direction polarization and relaxation polarization (electronic and ironic relaxation polarization).[12,13] We ascribe the high permittivity of nm-WO_3 to the ironic relaxation polarization. It is a character of ironic relaxation polarization that peaks exist in the spectrum of tgδ versus f,[10] which can be confirmed from Fig.5. The ironic relaxation polarization exists when the frequency is in the range of 10^2–10^5Hz, so nm-WO_3 exhibits high permittivity only when the frequency is low. At the same time, this kind of polarization mechanism makes the I–V curve asymmetric, as has been mentioned above.

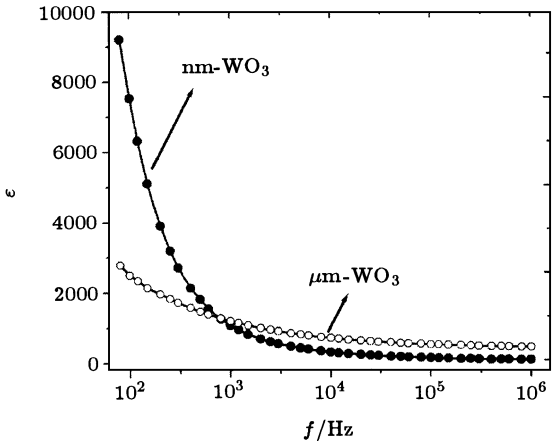


Fig.4. Frequency dependence of the permittivity for nm-WO_3 and μm-WO_3.

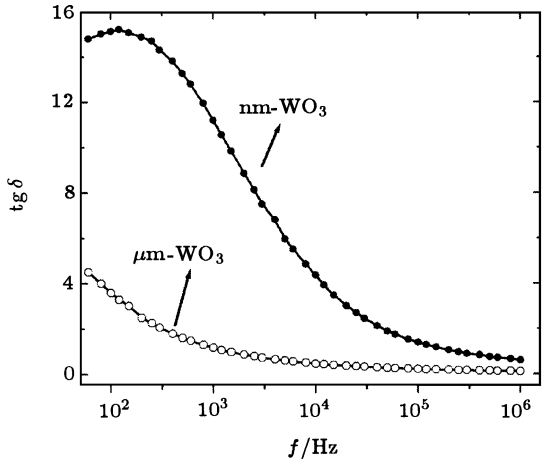


Fig.5. Frequency dependence of the dielectric loss tgδ for nm-WO_3 and μm-WO_3.

Moreover, crystallographic shear (CS) planes theory can also be introduced to explain the high permittivity of nm-WO_3. Oxygen deficiency (y) exists in ordinary WO_3, as has been mentioned above. With the increase of oxygen vacancies, the lattice tends to eliminate them by the CS planes mechanism. The CS planes are disordered when $y < 0.02$, but become interacted and tending to parallel when $y \geq 0.02$. The ordered degree increases with increasing y.[6,14] Tilley [15] first considered the importance of the high dielectric constant of some non-stoichiometric solids such as WO_3, Nb_2O_5 and TiO_2 for the formation and stability of CS planes. In nm-WO_3, its ordered degree of CS planes is higher than in μm-WO_3 because of its higher oxygen deficiency, resulting in a higher permittivity. Though the CS planes are important in some non-stoichiometric oxides especially for electrical properties, we did not find any published thesis discussing them in nanostructured materials.

4. Conclusion

Measurement of oxygen deficiency by the chemical method and EPMA analysis confirms that oxygen deficiency of nanocrystalline tungsten trioxide is higher than that of ordinary WO_3. The I–V curve is asymmetric, indicating that there is an additional polarization mechanism in nm-WO_3. Ironic relaxation polarization is believed to be the additional polarization mechanism, which can be confirmed by dielectric measurement. The ordered CS planes can be introduced to explain the high permittivity of the nanocrystalline tungsten trioxide.

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