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Impedance response of polycrystalline tungsten oxide

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ABSTRACT

Polycrystalline tungsten oxide (WO_3) pellets were prepared by conventional ceramic processing technology. The *ac small-signal* electrical data acquired in the frequency (f) range $100\,Hz \le f \le 1\,MHz$ at temperature (T) ranging the 31–100 °C revealed distinct semicircular relaxation in the impedance plane. This relaxation indicates device behavior originating from the grain boundaries. The lumped grain impedance associated with the device action remained too small to detect when the large resistance scale is realized. The semicircular relaxation is thermally activated indicating 0.58 eV as the activation energy for the relaxation time.

1. Introduction

The surface electronic structure of metal oxides play an important role for their use in many technological applications such as catalysis, chemical sensing, and high-efficiency solar cells [1–5]. The bulk electronic properties of tungsten oxide have been widely studied [6]. However, the surface electronic properties are little understood especially since the electronic properties of the surface can vary drastically from the bulk.

Tungsten oxide is intrinsically non-stoichiometric n-type semiconductor [6,7]. The defect states contribute to the formation of the device during the ceramic processing steps. These defect states need characterization via electrical measurements. The impedance measurement employing spectroscopic characterization approaches is popular for investigating novel devices and material systems [8]. These spectroscopic approaches include lumped parameter/complex plane analysis (LP/CPA) combining with the Bode plane analysis (BPA) becomes a powerful tool/technique for investigating polycrystalline semiconductors. This technique is especially valuable since it allows the deconvolution of the total impedance response of polycrystalline materials into their constituent components, such as bulk impedance (Z_{bulk}), grain and grain-boundary impedance (Z_g and Z_{gb}, respectively), and electrode (or contact) impedance (Z_{el}) according to their characteristic time constants.

The parallel-plate configuration is commonly used for bulk systems utilizing sinusoidal voltage as a function of measurement frequency. However, for many applications and situations it is the in-plane (surface) electrical properties rather than through-plane (bulk) properties of the sample that need to be characterized. The in-plane electrodes are of use in sensor applications, where interest is relative rather than absolute resistance values.

The purpose of this work is to investigate regular surface behavior of the polycrystalline tungsten oxide via impedance measurements, and subsequent representation of data in the impedance plane to shed light on the surface electronic characteristics.

2. Experimental

The commercial grade WO_3 (Alfa, 99.9% purity) powder was used as the starting material to make pellets (samples). In making cylindrical pellets of 14 mm diameter and thickness of about 2 mm 10 ton pressure was used. The pellets were sintered using a stepwise profile. First the heating rate was 2 °C/min, to a temperature of 400 °C from room temperature and held for 2 h, and then the heating rate was set 1 °C/min to reach a temperature of 800 °C for 2 h in ambient air. Then the pellets were cooled down to room temperature at the rate of 1 °C/min. The summary of the ceramic processing steps is identical to those in [9]. Silver paste was used as contacts/electrodes on the same surface with a finite

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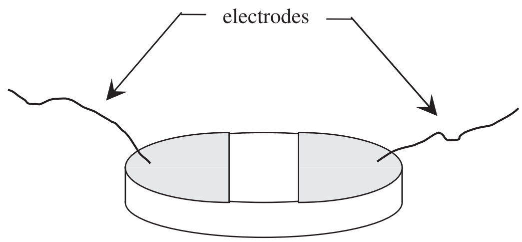

Fig. 1. The WO_3 pellet shows electroded regions with shade on the top surface having a finite gap between these two physical regions.

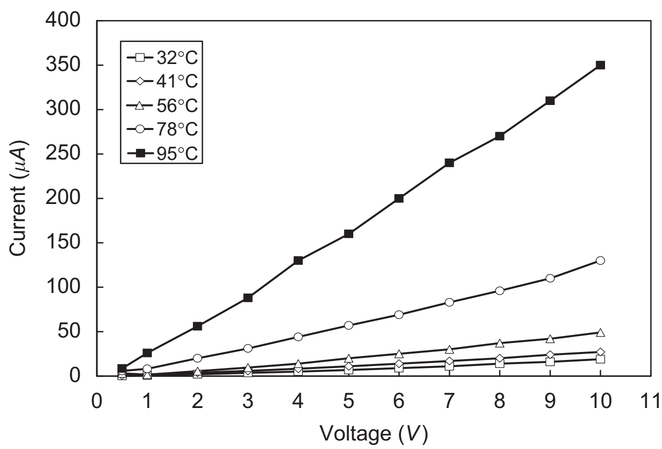

Fig. 2. Current–voltage (*I–V*) behavior of the tungsten oxide pellet surface.

gap of about 3 mm as depicted in Fig. 1. The surface current–voltage (*I–V*) behavior of the tungsten oxide sample depicted in Fig. 2 was obtained using the usual measurement set-up via power supply and electrometer at various temperatures.

The impedance measurement set-up consists of a kiln (hot-plate oven) and a QuadTech 7600 precision LCR meter interfaced with a computer via GPIB to USB2 using LabView software. The temperature was monitored using a *Type K* thermocouple attached to a Cole–Parmer temperature controller (Digi-Sense). The ambient temperature of the sample was varied from room temperature (≈31 °C) to 100 °C. A schematic display of the impedance measurement set-up of the device under test (DUT) was displayed recently [9]. The *ac small-signal* voltage was 1 V peak to peak, and the acquired *ac* data were reproducible within small variation of the signal voltage. The automated data were recorded continuously from 100 Hz to 1 MHz at a given temperature. The *ac small-signal* voltage is experienced in the resistive domain within the material system. Thus, high-resistance region will experience high electric field while low-resistance region will experience low electric field. Thus, the *electric field falling region* can be referred to as the basis of the magnitude of resistance of the physical regions within the microstructure of polycrystalline materials [9–13].

3. Results and discussion

Fig. 2 shows *low sub-ohmic* to *minor non-ohmic* behavior of tungsten oxide at various temperatures. Each curve coincides with the origin implying no current flow at 0 V. Direct extrapolation of the curve may not get through the origin because of the slight non-linear response. This type of response is identical to the previous studies [3,6]. The *ac small-signal* electrical data are converted to the terminal impedance in the form

$$Z* = Z' - jZ'' = R_s - j[1/(\omega C_s)], \tag{1}$$

where the impedance plot refers to the real part displayed on the *x*-axis and imaginary part displayed on the *y*-axis.

The temperature dependence of the dc resistance is shown in Fig. 3. The displayed response suggests that there is an inflection in the thermal behavior indicating eruption of more than one kind of behavior for the initial mechanism. However, on the basis of the fitted curve some sort of singular activation energy of 0.336 eV may be obtained. The presence of an inflection in the Arrhenius plot is a plausible aspect for the polycrystalline sample when each contributing equivalent circuit element represented by the resistance–capacitance (*R–C*) relaxation does not reflect consistent or systematic dominance with increase or decrease in temperature. Thus, either *R* or *C* can increase or decrease with increase or decrease in temperature in a pattern shown in Fig. 3. This type of thermal sensitivity on constituting equivalent circuit elements may cause inflection in the origin of the dc resistance. The dual nature of the thermal behavior of the dc resistance via inflection or non-linear behavior in the Arrhenius plot indicates emergence of potential trapping contribution from the grain-boundary regions where a large portion of the applied voltage is experienced. This is considered for the polycrystalline material apart from the thermal carrier contribution for the charge transport attributed to the dc resistance [14].

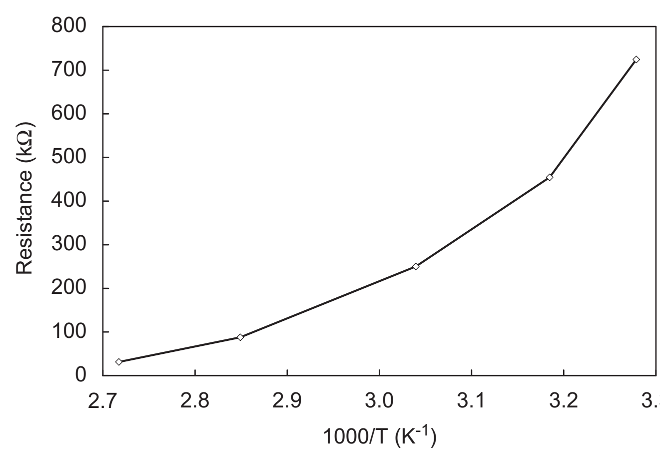

Fig. 3. Temperature dependence of the dc resistance obtained from the current–voltage behavior.

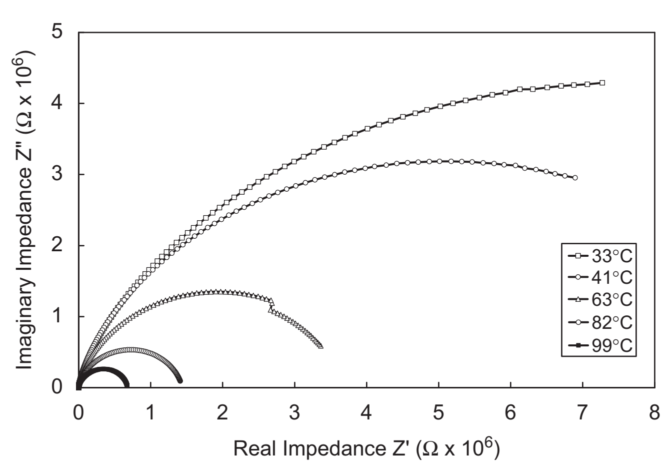

Fig. 4. Impedance plot of tungsten oxide sample at various temperatures.