Semiconducting Properties of Cold Sintered V_2O_5 Ceramics and Co-sintered V_2O_5 -PEDOT:PSS Composites

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Abstract

Recently we established a sintering approach, namely Cold Sintering Process (CSP), to densify ceramics and ceramic-polymer composites at extraordinarily low temperatures. In this work, the microstructures and semiconducting properties of V_2O_5 ceramic and $(1-x)V_2O_5$ - x PEDOT:PSS composites cold sintered at 120 °C were investigated. The electrical conductivity (25 °C), activation energy (25 °C) and Seebeck coefficient (50 °C) of V_2O_5 are 4.8×10^{-4} S/cm, 0.25 eV, and -990 μ V/K, respectively. The conduction

mechanism was studied by the hopping model. A reversible metal-insulator transition (MIT) was observed with V_2O_5 samples exposed to a N_2 atmosphere, whereas in vacuum atmosphere no obvious MIT could be detected. With the addition of 1-2 Vol% PEDOT:PSS, the electrical conductivity (50 °C) dramatically increases from 10^{-4} to $10^{-3}\sim 10^{-2}$ S/cm and the Seebeck coefficient (50 °C) shifts from -990 to -(600~250) μ V/K. All the results indicate that CSP may offer a new processing route for the semiconductor electroceramic development without a compromise to the all-important electrical properties.

Keywords: Cold Sintering Process; Oxide Semiconductor; V_2O_5 ; V_2O_5 -PEDOT:PSS Composite; Metal-Insulator Transition

1. Introduction

Vanadium oxides across different stoichiometries are known for a variety of crystal structures, physical and chemical properties [1, 2]. Part of this diversity comes from the broad range of oxidation states, from V^{+2} to V^{+5} . Among them, vanadium pentoxide V_2O_5 is the most stable compound. To reduce the environmental foot print and damage from fossil fuels, it will be imperative to develop sustainable energy policies for manufacturing and also develop new high energy and high power density devices. Oxide semiconductors are promising in energy related applications, such as energy storage and energy saving. As a wide bandgap semiconductor, V_2O_5 is of considerable interest in many technological

applications, such as gas and humidity sensors, catalyst supports, electrical and optical switching devices, electrochromic devices, thermoelectric devices, and lithium-ion batteries [2-7]. For the temperature dependent properties, there is a controversy: some researchers believe that V_2O_5 do not exhibit a metal-insulator transition (MIT) [8], whereas other groups have reported that V_2O_5 undergoes a MIT at 257 °C [5] and Blum et al. have reported that the MIT of V_2O_5 only occurs across the surface at 77-127 °C [9].

Generally speaking it is difficult to prepare well-sintered V_2O_5 ceramics with high densities (>90%) [10]. The conventional thermal sintering at 450-660 °C yields low dense V_2O_5 ceramics. With the combination of hot pressing (630°C/2h/30MPa) and hot isostatic pressing(630°C/1h/196MPa), Honma et al. succesfully fabricated well-sintered V_2O_5 ceramics with the relative density of 97.7% [11]. Recently, we developed a new sintering technique, namely Cold Sintering Process (CSP) [10, 12-15]. A number of materials, including oxides, carbonates, bromides, fluorides, chlorides and phosphates, can all be sintered to 80-99% theoretical density at an extraordinarily low temperatures, <300 °C. The densification occurs with the assitant of a transient aqueous solution by a mediated dissolution-precipitation process under a uniaxial pressure. CSP provides a simple and energy-saving route to sinter dense V_2O_5 ceramics. With CSP at 120 °C for 20min, V_2O_5 can be sintered to >90% of the theoretical densities.

The low processing temperature of the CSP technique also makes it possible to fabricate ceramic-polymer composites with high volume fraction of ceramics.[10] Our

previous work demonstrated the potential of CSP in the sintering of V_2O_5 -(poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate)) (PEDOT:PSS) composites [10]. In this study, cold sintered V_2O_5 ceramics and V_2O_5 -PEDOT:PSS composites are discussed in detail to demonstrate the feasibility of CSP in semiconductor oxide applications. The microstructures and the temperature dependences of electrical conductivity, activation energy controlling electronic transport mechanism, and thermoelectric properties such as the Seebeck coefficient and power factor were also investigated.

2. Experimental

Densified V_2O_5 ceramics and $(1-x)V_2O_5$ - x PEDOT:PSS composites were prepared by CSP at 120 °C for 20 min under a pressure of 350 MPa, as described in the previous work [10, 12]. The X-ray diffraction (XRD) data were collected using PANalytical Empyrean XRD system at 45 KV and 40 mA with Cu K α radiation with a scan rate of 0.026 over a diffraction scan range between 10 to 70 degrees. The powders and fracture surfaces of ceramics were observed with a field emission scanning electron microscope (FESEM, FEI, NanoSEM 630). The Focused Ion Beam (FIB) cross sections were obtained by FEI Helios NanoLab 660 FIB/SEM. The transmission electron microscope (TEM) samples were prepared by the same FIB system and the TEM analysis was done by FEI Talos F200X. For the measurement of temperature dependence of electrical conductivity (σ),

the cold sintered disks were cut into bars with a dimension of 10×2×1 mm and polished. Pt electrodes were deposited and 4 Ag wires were attached on the bars with Ag epoxy (Epo-tek H20E). The electrical conductivity was determined in the temperature range of 25-500 °C using a four probe technique, with a Keithley 2700 Integra series digital multimeter and a tube furnace. The measurement was performed in N₂ and vacuum (<8 mbar) atmospheres with a heating rate of 1 °C/min and a cooling rate of 1 °C/min. For thermoelectric measurements, the cold sintered samples were cut into bars with a dimension of 10×2×2 mm and polished. The Seebeck coefficient (S) and corresponding electrical conductivity were obtained using LSR-3 system (LINSEIS Messgeräte GmbH). The measurement was performed in a He atmosphere with a pressure of 1 bar. The Seebeck coefficients were calculated using the slope of Seebeck voltage (ΔV) and temperature gradient (ΔT). The thermoelectric power factor (PF) was calculated as follows: $PF=S^2\sigma$.

3. Results and Discussions

V₂O₅ has a layered crystal structure with orthorhombic symmetry (Pmmn). There is no obvious impurity phase in the X-ray diffraction data of the V₂O₅ cold sintered samples processed at 120 °C under a pressure of 350 MPa, and furthermore the peaks can be readily indexed to the orthorhombic structure [12]. The microstructures of V₂O₅ raw powders and typical V₂O₅ ceramics after cold sintering are contrasted and shown in Fig. 1.

It is seen that the grain size of cold sintered ceramics is almost the same as the particle size of raw powders. CSP of V_2O_5 ceramics is a very fast process (~20 min) at an extraordinarily low temperature of 120 °C, which is not sufficient for notable grain growth in this system. The phenomenon of grain growth limitation of V_2O_5 is similar to that of alkali molybdates [12]. The SEM images of the FIB cross sections of V_2O_5 ceramics are shown in Figure S1 (supplementary information). Only a small amount of pores can be observed revealing that the cold sintered V_2O_5 samples have a relatively high density.

The microstructural details of cold sintered V_2O_5 ceramics were further investigated by TEM analysis. The bright-field TEM micrographs of V_2O_5 are shown in Fig. 2. A small amount of amorphous phase occurs around the grain boundaries. During CSP of V_2O_5 ceramics, a small amount of deionized water was added to the powder forming a liquid phase, which aids densification by a mediated dissolution-precipitation process. Therefore, an amorphous phase may exist in the cold sintered V_2O_5 samples, which is similar to the results of other cold sintered ceramics [12, 14]. However, most of the grain boundaries have no amorphous phase, indicating that the cold sintered V_2O_5 ceramics are highly crystalline. Additionally, nanometer-sized crystals can be observed in the amorphous phase, as shown in Fig. 2d, demonstrating that dissolution-precipitation process dominates the sintering mechanism.

The densification of V_2O_5 ceramic by CSP can be further confirmed by the data

listed in Table 1. With CSP at 120 °C for 20min, V₂O₅ can be well densified (>90%) and the electrical conductivity, activation energy and Seebeck coefficient are all comparable to those reported in the literature with traditional high temperature processes. The preparation methods and conditions play an important role in the electrical conductivity of V₂O₅. The presence of V⁴⁺ in V₂O₅ can also change the electrical conductivity [11]. From Table 1, it is seen that the bulk amorphous V₂O₅ prepared by splat-cooling has a low room temperature (RT) conductivity of 6.5×10⁻⁶ S/cm, while the single crystal has a high RT conductivity of 10⁻³~10⁻⁴ S/cm. The RT conductivity of cold sintered V₂O₅ ceramic (4.8×10⁻⁴ S/cm) is higher than that conventionally sintered ceramics at 450 °C for 24h (5×10⁻⁵ S/cm), and similar to that of hot pressed V₂O₅ ceramics (10⁻⁴ S/cm) and single crystals (10⁻³~10⁻⁴ S/cm), as shown in Table 1. There are also many research groups working on V₂O₅ thin films, and most of these efforts reported RT conductivities in the range of 10⁻⁴~10⁻⁷ S/cm [6, 16, 17]. The electrical conductivity of V₂O₅ bulk ceramic cold sintered at 120 °C is comparable to the data shown in these literatures. V₂O₅ is an n-type semiconductor, and the Seebeck coefficient is negative. The V₂O₅ ceramic prepared by CSP has a negative Seebeck coefficient of around -990 μV/K at around 50 °C, which is comparable to previous reported Seebeck coefficients, including traditional fired bulk ceramics (-1130 μV/K at 25 °C), single crystals (-900 ~ -1600 μV/K at 50 °C) and thin films [6, 17] (-385 ~ -540 μV/K at 25 °C).

Figure 3a presents the electrical conductivity of V₂O₅ ceramic in the temperature

range of 25-250 °C. The data were recorded four times with 2 heating and 2 cooling profiles. The electrical conductivity in the first heating profile is a little smaller than that in the cooling and the second heating profiles, which may result from the changes of intergranular amorphous phases. The heat treatment at higher temperatures can change the amount of amorphous phase, which increases the electrical conductivity of V₂O₅. Since all the electrical conductivities in the cooling and the second heating profiles are similar, one of these curves is selected for a more detailed study of the nature of the conduction mechanism in V₂O₅. It is well known that the small polaron hopping model follows the equation [18, 19]:

$$\sigma = \sigma_0 e^{-\Delta E/kT} = \frac{A}{T} e^{-\Delta E/kT} \quad (1)$$

Where σ is the electrical conductivity; σ_0 is the pre-exponential factor; A is a constant for one material; T is the absolute temperature; ΔE is the activation energy for hopping; k is the Boltzmann constant. As shown in Fig. 3b, $\ln(\sigma T)$ decreases linearly with $1/T$, indicating that the small polaron hopping dominates the conduction mechanism of V₂O₅. The activation energy calculated from the slop of the curve of $\ln(\sigma T)$ vs $1/T$ is around 0.25 eV.

The electrical conductivity of a V₂O₅ ceramic from 25 °C to 500 °C in N₂ is shown in Fig. 4a. The conductivity in the first heating profile is quite different from that in the cooling and the second heating profiles. The measurement is in N₂ atmosphere and V⁵⁺ can be reduced to V⁴⁺. The XRD patterns shown in Fig. 5 indicate that the reduction

occurs on the surface of V_2O_5 ceramic. After the first heating profile (500 °C treatment), the color of V_2O_5 surface changes from brown to dark blue, and vanadium oxides with V^{4+} ions such as VO_2 , V_6O_{13} , and V_3O_7 are detected. After polished, the color of V_2O_5 surface returns to brown and only a small amount of V_3O_7 is detected. According to the oxygen distribution shown in Figure S2 (supplementary information), **we estimate that the thickness of the reduced oxide layer is less than 50 μm .** From the XRD results, it can be inferred that V_2O_5 contributes to the internal resistance (R_i) and reduced V_2O_5 with V^{5+} and V^{4+} ions contributes to the surface resistance (R_s). A parallel system is formed by R_s and R_i , which results in a decrease of the total resistance (R_t). Therefore, the conductivity in the cooling profile and the second heating profile is 1-2 orders of magnitude larger than that in the first heating profile.

From **Fig. 4a**, it is also seen that, after 500 °C treatment (first heating profile), the valance state of V becomes stable and the electrical conductivities in the cooling and sencond heating profiles are similar. A reversible MIT can be observed at ~62 °C and the conductivity increases by 1-2 orders of magnitude. It is known that VO_2 has a MIT around 67 °C [20], which is similar to the MIT observed in **Fig. 4a**, revealing that VO_2 on the surface of V_2O_5 sample dominates the MIT.

Figure 4b plots the electrical conductivity of V_2O_5 ceramic from 25 °C to 500 °C in vacuum (<8 mbar). Similar to the result shown in **Fig. 4a**, the electrical conductivity of V_2O_5 ceramic increases after the first heating profile. Some V^{5+} ions reduces to V^{4+} ions

and V_6O_{13} is observed in the XRD pattern of unpolished surface of V_2O_5 ceramic, as shown in Fig. 5. After polished, no significant impurity phase can be detected, indicating that the reduction only occurs on the surface of V_2O_5 ceramic. The parallel system discussed above results in the increase of electrical conductivity after the first heating profile. After 500 °C treatment, the valance state of V becomes stable and the electrical conductivities in the cooling and second heating profiles are similar. But in this case, no obvious MIT can be observed, revealing that neither V_2O_5 nor V_6O_{13} have MIT in the temperature range of 25 °C and 500 °C.

$(1-x)V_2O_5$ - x PEDOT:PSS composites can be readily sintered to >90% theoretical density with CSP at 120 °C for 20 min under a pressure of 350 MPa [10]. The microstructures of 98.4 V_2O_5 -1.6PEDOT:PSS composites are shown in Figure S1 (supplementary information) and Figure 6. It is seen that the 98.4 V_2O_5 -1.6PEDOT:PSS composites have a high density and the grain size of V_2O_5 in the composites is similar to that in the pure V_2O_5 ceramics. It is also observed that the V_2O_5 grains may be surrounded by polymer (PEDOT:PSS) and amorphous-phase, as shown in Figure 6b,c.

The temperature dependent electrical conductivities of $(1-x)V_2O_5$ - x PEDOT:PSS composites with small x values are shown in Fig. 7. For each sample, the data were collected four times with 2 heating and 2 cooling profiles in the temperature range of 25-250 °C, and the results are similar to that of V_2O_5 ceramic discussed above (Fig. 3a). The cooling curves are selected to study the conduction mechanism in

(1-x)V₂O₅-xPEDOT:PSS composites. As shown in Fig. 7b, there is a linear relationship between $\ln(\sigma T)$ and $1/T$, suggesting that the small polaron hopping dominates the transport properties of (1-x)V₂O₅-xPEDOT:PSS composites. The activation energy decreases from 0.25 eV to 0.22 eV when x value increases from 0 to 1.6 Vol%.

Figure 8 presents the thermoelectric properties of (1-x)V₂O₅-xPEDOT:PSS composites. With the addition of 1-2 Vol% PEDOT:PSS, the electrical conductivity dramatically increases from 10^{-4} S/cm to 10^{-3} ~ 10^{-2} S/cm at 50 °C, and the Seebeck coefficient drops from -990 μ V/K to -(600~250) μ V/K at 50 °C. The power factor is dominated by both electrical conductivity and Seebeck coefficient. Therefore, the power factor at 50 °C of the (1-x)V₂O₅-xPEDOT:PSS composites increased from 5.5×10^{-4} μ W/cmK² to 1.1×10^{-3} μ W/cmK² (0.8%PEDOT) and 1.6×10^{-3} (1.6%PEDOT) μ W/cmK² by adding 1-2 Vol% PEDOT:PSS.

4. Conclusions

This study shows details of a CSP applied to a semiconductor oxide in terms of the relative properties under this process. The microstructural analysis of the V₂O₅ ceramic reveals that the densification occurs under the CSP condition and the grain growth is limited. Owing to the dissolution-precipitation process, a small amount of amorphous phase occurs around the grain boundaries. The electrical conductivity (25 °C), activation energy (25 °C) and Seebeck coefficient (50 °C) of V₂O₅ ceramic are 4.8×10^{-4} S/cm, 0.25

eV, and $-990 \mu\text{V/K}$, respectively, those are comparable to the data in the literature. The temperature dependence of electrical conductivity indicates that the small polaron hopping model dominates the conduction mechanism. After a heat treatment of 500°C in N_2 atmosphere (the first heating profile), the surface of V_2O_5 reduces to vanadium oxides with V^{5+} and V^{4+} ions and a reversible metal-insulator transition at $\sim 62^\circ\text{C}$ can be observed. Whereas under exposure to a vacuum atmosphere, no obvious MIT can be observed, revealing that V_2O_5 does not have MIT in the temperature range of 25°C and 500°C . With the addition of 1-2 Vol% PEDOT:PSS, the electrical conductivity (50°C) dramatically increases from 10^{-4} to $10^{-3}\sim 10^{-2} \text{ S/cm}$, the Seebeck coefficient (50°C) shifts from -990 to $-(600\sim 250) \mu\text{V/K}$, and the power factor (50°C) increases 2-3 times. Overall, it is anticipated that CSP is a potential process to sinter semiconductor ceramics or ceramic-polymer composites at extremely low temperatures, which provides a new route for the developments of oxide semiconductors.

Acknowledgements

This work was supported by the National Science Foundation, as part of the Center for Dielectrics and Piezoelectrics under Grant Nos. IIP-1361571 and 1361503. The authors would like to thank Steven E. Perini (Materials Research Institute, The Pennsylvania State University) for his help in the measurements of temperature dependent conductivity under vacuum. The authors also thank Jonathan A. Bock (Materials Research Institute,

The Pennsylvania State University) for his help in the Seebeck coefficient measurements.

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Table and figure captions

Table 1 Densities (RT), electrical conductivities (RT), activation energies (RT) and seebeck coefficients (RT or 50 °C) of V_2O_5 ceramic/crystal prepared by different processes. (ST: Sintering temperature (For single crystal and amorphous ceramic, ST represents the sample preparation temperature), ρ : Density, σ : Electrical conductivity, ΔE : Activation energy, S: Seebeck coefficient, CSP: Cold Sintering Process, HP: Hot press, TS: Thermal sintering, CM: Casting the melt into metal molds, SC: Splat-cooling).

Fig. 1 SEM images of V_2O_5 raw powder (a) and fracture surface of V_2O_5 ceramic after CSP at 120 °C for 20 min (b). The Focused Ion Beam (FIB) milled cross sections are shown in Figure S1 (supplementary information).

Fig. 2 Bright-field transmission electron microscope (TEM) images of V_2O_5 ceramic cold sintered at 120 °C. (a) Overview of grain morphology. (b) Crystalline grain boundaries. (c) Crystal/amorphous-phase boundaries. (d) Crystal/amorphous-phase boundaries with the

appearance of nanometer crystals. The nanometer crystal was marked by a circle.

Fig. 3 The electrical conductivity of cold sintered V_2O_5 ceramic from 25 °C to 250 °C in N_2 (a) and the natural log of electrical conductivity-temperature product $\ln(\sigma T)$ against reciprocal thermal energy $1/kT$ (b).

Fig. 4 The electrical conductivity of cold sintered V_2O_5 ceramic from 25 °C to 500 °C in N_2 (a) and vacuum (b).

Fig. 5 X-ray diffraction patterns of unpolished and polished surfaces of V_2O_5 ceramic after 500 °C treatment in N_2 and vacuum (The heating rate of 500 °C treatment is 1°C/min, which is the same as the heating rate in the measurement of temperature dependent conductivity).

Fig. 6 The SEM image (a), HAADF image (b) and EDS map (c) of $98.4V_2O_5-1.6PEDOT:PSS$ composites after CSP at 120 °C for 20 min. The box in the HAADF micrograph shows where the EDS map was taken. The Elemental V is shown in red and elemental C is shown in green.

Fig. 7 The electrical conductivity of cold sintered $(1-x)V_2O_5-xPEDOT:PSS$ composites from 25 °C to 250 °C in N_2 (a) and the natural log of electrical conductivity-temperature product $\ln(\sigma T)$ against reciprocal thermal energy $1/kT$ (b).

Fig. 8 The Seebeck coefficients of $(1-x)V_2O_5-xPEDOT:PSS$ composites.

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Process	ST (°C)	ρ (g/cm ³)	σ (S/cm)	ΔE (eV)	S (μV/K)
Polycrystalline Bulk (CSP)	120	3.03 (90.2%)	4.8×10^{-4}	0.25	-990 (50°C)
Polycrystalline Bulk (HP)[11]	630	3.28 (97.7%)	10^{-4}	0.18	
Polycrystalline Bulk (TS)[4]	450	2.16 (64%)	5×10^{-5}	0.21	-1130 (25°C)
Polycrystalline Bulk (CM)[21, 22]	800		$\sim 10^{-4}$	0.2	
Single Crystal[21, 22]	800	3.357	10^{-4} (b axis) $\sim 10^{-3}$ (a, c axis)	0.2	
Single Crystal [23]	750		$8.3 \times 10^{-4} \sim 8.8 \times 10^{-4}$ (c axis)	0.17~0.189	
Single Crystal[24]			10^{-4} (b axis) $\sim 10^{-3}$ (c axis)	0.27	-(900~1600) (50°C)
Amorphous Bulk (SC)[25]	800		6.5×10^{-6}	0.35	

Figures

Fig. 1 SEM images of V₂O₅ raw powder (a) and fracture surface of V₂O₅ ceramic after CSP at 120 °C for 20 min (b). **The Focused Ion Beam (FIB) milled cross sections are shown in Figure S1 (supplementary information).**

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Fig.3 The electrical conductivity of cold sintered V_2O_5 ceramic from $25\text{ }^{\circ}\text{C}$ to $250\text{ }^{\circ}\text{C}$ in N_2 (a) and the natural log of electrical conductivity-temperature product $\ln(\sigma T)$ against reciprocal thermal energy $1/kT$ (b).

Fig. 4 The electrical conductivity of cold sintered V_2O_5 ceramic from 25 °C to 500 °C in N_2 (a) and vacuum (b).

Fig. 5 X-ray diffraction patterns of unpolished and polished surfaces of V_2O_5 ceramic after 500 °C treatment in N_2 and vacuum (The heating rate of 500 °C treatment is 1°C/min, which is the same as the heating rate in the measurement of temperature dependent conductivity).

Fig. 6 The SEM image (a), HAADF image (b) and EDS map (c) of 98.4V₂O₅-1.6PEDOT:PSS composites after CSP at 120 °C for 20 min. The box in the HAADF micrograph shows where the EDS map was taken. The Elemental V is shown in red and elemental C is shown in green.

Fig. 7 The electrical conductivity of cold sintered $(1-x)\text{V}_2\text{O}_5$ - $x\text{PEDOT:PSS}$ composites from 25 $^{\circ}\text{C}$ to 250 $^{\circ}\text{C}$ in N_2 (a) and the natural log of electrical conductivity-temperature product $\ln(\sigma T)$ against reciprocal thermal energy $1/kT$ (b).

Fig. 8 The Seebeck coefficients of $(1-x)\text{V}_2\text{O}_5\text{-}x\text{PEDOT:PSS}$ composites.