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Oxygen gas-sensing behaviour of V_2O_5–SnO–TeO_2 glass

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The d.c. conductivity, σ, and the oxygen gas-sensing behaviour of V_2O_5–SnO–TeO_2 glass prepared by press-quenching were studied in argon and oxygen gas atmospheres at temperatures ranging from 303–473 K. The glass of $50V_2O_5 \cdot 20SnO \cdot 30TeO_2$ (mol %) was n-type semiconducting. The high-temperature conductivity was lower in oxygen and higher in argon than that in air. This was explained by the V^{4+} ions in the glass being oxidized by oxygen which had diffused into the glass, resulting in an increase in V^{5+} with time. The experimental relationship between σ and oxygen partial pressure, P_{O_2}, agreed quantitatively with the theoretical relation $\sigma \propto P_{O_2}^{-1/4}$. Changes in conductivity by switching the atmospheres between oxygen and argon gases were found to be reproducible. From the data of these dynamic changes, the oxygen gas sensitivity, S, at 473 K was obtained to be 1.3 in oxygen atmosphere. The dynamic changes could be quantitatively explained by an oxygen diffusion model. Throughout these discussions, the present tellurite glass was found to possess a potential applicability as an oxygen gas sensor.

1. Introduction

Semiconducting ceramics such as SnO_2 (+Ag) [1], SnO_2 (+metal oxides) [2], ZnO [3], SnO_2 (+Pd) [4], WO_3 [5], ZnO:Ga [6] have been widely studied as a gas sensor. The electrical conductivity of these n-type semiconductive gas sensors increased on exposure to reducing gases at high temperature. In a CoO [7] (p-type semiconductor) gas sensor, the conductivity increased for oxidizing gases. Recently, semiconducting glasses containing transition metal oxides, such as V_2O_5–SrO–Sb_2O_3 glass [8], have also been found to have oxygen gas-sensing properties; the gas-sensing mechanism was attributed to the $V^{4+} \rightarrow V^{5+}$ produced by oxygen diffusion into the glass under an oxygen atmosphere, resulting in a decrease in its conductivity. Generally, transition metal oxide glasses [9–17] are known to be semiconducting, and the electrical conduction was interpreted by the small polaron hopping (SPH) model [18, 19]. We reported the electrical properties of vanadium tellurite glasses in the system V_2O_5–R–TeO_2 (R = Sb_2O_3 [7], SnO [10], Bi_2O_3 [11] and ZnO [12]). The electrical conduction of these glasses was confirmed to be due to SPH between vanadium ions and was adiabatic SPH for $V_2O_5 \geqslant 50$ mol %, and non-adiabatic SPH for $V_2O_5 < 50$ mol %. The d.c. electrical conductivity of these glasses was almost determined by the mobility, μ [9–12]. Because tellurite glasses can transmit infrared rays [20], their optical applications [21–23] were investigated. However, few reports have been found on electrical application of tellurite glasses [24]. We expected tellurite glasses with a conductivity as high as V_2O_5–SrO–Sb_2O_3 glass [8] to have a feasibility as an oxygen gas sensor.

In the present study, variations in d.c.-conductivity of $50V_2O_5 \cdot 20SnO \cdot 30TeO_2$ glass (mol %) were investigated in argon and oxygen gas atmospheres at temperatures ranging from 303–473 K, and oxygen gas sensitivity, S, was determined, because this tellurite glass has a high conductivity ($\sigma = 2.05 \times 10^{-5}$–$3.71 \times 10^{-4}$ S cm^{-1} at 473 K [10]). We also examined the relationship between σ and oxygen partial pressure, P_{O_2}, because there has been no such work published on semiconductive glasses, like semiconducting ceramics [25–28].

2. Experimental procedure

The glass sample used for the experiment was $50V_2O_5 \cdot 20SnO \cdot 30TeO_2$ (mol %), which was the most conductive as an n-type semiconductor [10]. The process for preparation of the glass sample was described elsewhere [10]. Regent grade 99.9%V_2O_5, 99.9%SnO and 99.99%TeO_2 were mixed for 20 min in the prescribed composition and a batch (5 g) was melted in air in a porcelain crucible in an electrical furnace, at 750 °C for 1 h. The melt was then poured on to a copper block to prepare the quenched glass sample. Thus, a glass sample of square plate, 1.0 mm thick, 4 cm^2 square, was obtained. After dry crushing of the glass sample in air in a mortar, a pellet of the glass powder was prepared by pressing in air at 277 MPa. The sample was then sintered in air for 3 h at a temperature of 220 °C, lower than $T_g = 228$ °C

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[10] of the glass. The powder making and sintering were carried out to increase the surface area of the glass. Finally, a sample of disc plate with 10 mm diameter and 2 mm thick was obtained; this was confirmed to be amorphous from X-ray diffraction analysis. The four-point probe method was employed to determine d.c. electrical conductivity at temperatures from 303–473 K where 1 μA d.c. current was applied during the measurement. Electrodes were made with gold paste. The heating rate during the measurement was 1 K min^{-1}. D.c. conductivity on the same glass sample in different runs agreed within 0.1%. Samples of the same composition from different batches gave agreement within 5% at room temperature conductivity. Dry argon or oxygen gas was flowed constantly during the d.c. resistance measurements. Each atmospheric gas was flowed independently into the furnace chamber at a flow rate of 0.3–1.0 l min^{-1}. Gas sensitivity, *S*, was defined as the ratio of initial resistivity to that of saturated resistivity in an atmospheric gas. The particle size of the pellet glass was determined by scanning electron microscopic (SEM) observation of the pellet surface. Glass density was measured at 293 K with a Gay–Lussac pycnometer using toluene.

3. Results

Fig. 1 shows a scanning electron micrograph of the surface of the pellet. The particle size of the glass is within 5 μm. The measured density of the pellet glass was 3.168 g cm^{-3}, and smaller than the bulk density (4.014 g cm^{-3}) [10] for $50V_2O_5 \cdot 20SnO \cdot 30TeO_2$ glass. The ratio of the pellet density to the bulk one was estimated to be 0.78. Thermoelectrical power measurement indicated the glass to be n-type semiconductor. No d.c. polarization was observed.

Fig. 2 shows the temperature dependence of the d.c. conductivity, σ, of the glass in argon and oxygen atmospheres. The conductivity data are the saturated values in the time dependence under each gas atmosphere obtained for a gas flow rate of 1 l min^{-1}. The conductivity was saturated on flowing the gases for 6 h. From Fig. 2, σ in oxygen gas was found to be lower than that in an argon atmosphere. σ in air was determined to be 1.71×10^{-3} S cm^{-1} at 473 K. σ in argon gas was 1.96×10^{-3} S cm^{-1} and under an oxygen atmosphere $\sigma = 1.10 \times 10^{-3}$ S cm^{-1} at 473 K. This indicates that an oxygen atmosphere decreases σ, while an argon gas atmosphere increases σ.

Fig. 3 shows variations in conductivity at 473 K of the glass under different oxygen partial pressures, $P_{O_2} = 0.15$, 0.20 and 0.35 atm. The conductivity was saturated at each P_{O_2} for 1 h, and the larger P_{O_2} caused a reduction in the saturated conductivity.

In Fig. 4, the changes in conductivity of the glass with time, *t*, elapsed after introducing the gases on alternate switching of atmospheric argon and oxygen gases every 1 h at (a) 473, (b) 453 and (c) 433 K are shown. σ increased with the elapsed time in argon atmosphere, while in oxygen atmosphere, σ decreased with time. From this, the changes in conductivity were found to be reproducible on alternate switching of argon and oxygen gases.

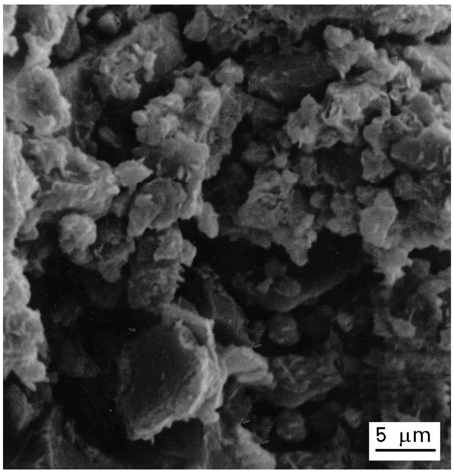

Figure 1. Scanning electron micrograph of the surface of the pellet: $50V_2O_5 \cdot 20SnO \cdot 30TeO_2$ glass (mol %).

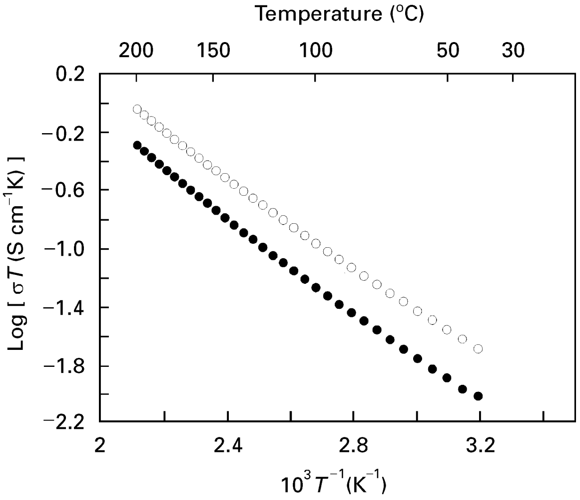

Figure 2. Temperature dependence of conductivity for $50V_2O_5 \cdot 20SnO \cdot 30TeO_2$ glass (mol %) in different gas atmospheres: (○) argon gas ($r^2 = 0.9985$, r = correlation coefficient), (●) oxygen gas ($r^2 = 0.9985$). The least square fitting was carried out at temperatures between 303 and 473 K.

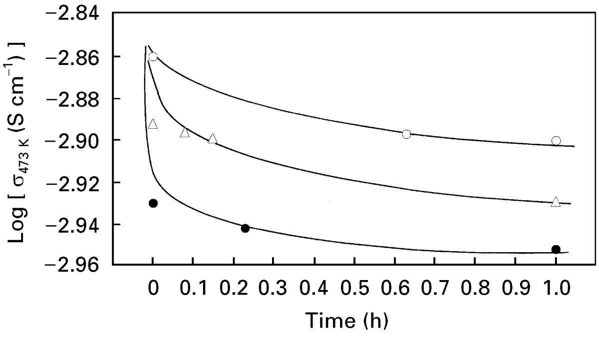

Figure 3. Variations in conductivity of $50V_2O_5 \cdot 20SnO \cdot 30TeO_2$ glass (mol %) as a function of oxygen partial pressure P_{O_2} at 473 K. (○) $P_{O_2} = 0.15$ atm, (△) $P_{O_2} = 0.20$ atm, (●) $P_{O_2} = 0.35$ atm. The lines are drawn as a guide to the eye.

Gas sensitivity, *S*, was examined from the data of Fig. 2, and $S = 1.8$ was obtained at 473 K. This *S* value is very low compared with the case of WO_3 ($S = 10$ for NO) [5], ZnO:Ge ($S = 110$ for NO_2) [6]

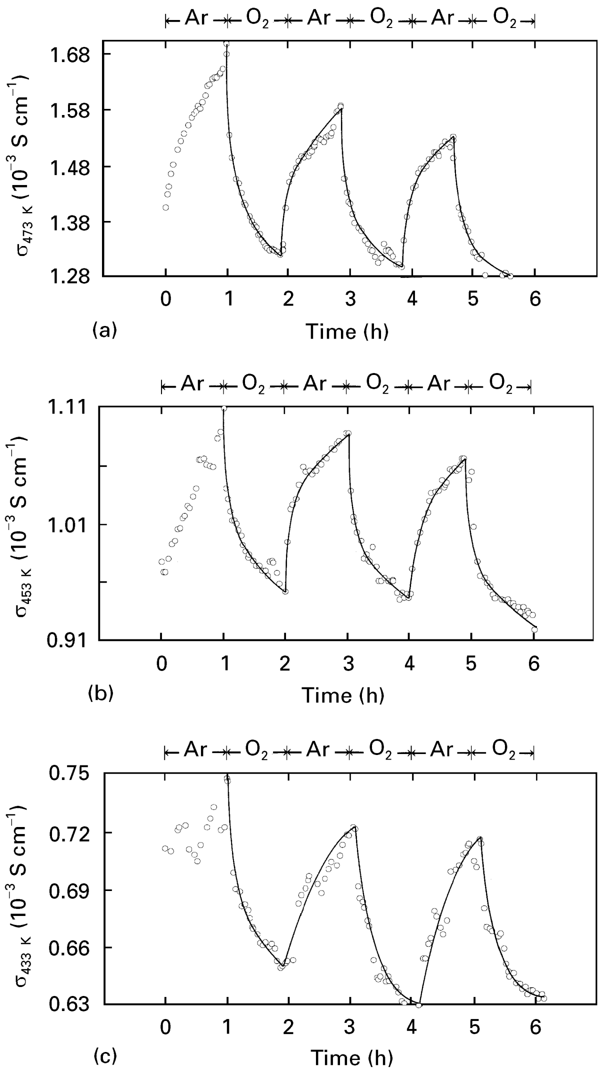

Figure 4. Changes in conductivity of $50V_2O_5 \cdot 20SnO \cdot 30TeO_2$ glass with time at (a) 473 K, (b) 453 K and (c) 433 K on alternate switching of argon and oxygen gases. The solid lines were calculated using Equations 8 and 11.

and ZnO ($S = 19$ for C_3H_8) [28]. In addition, the S value determined from the data of Fig. 4a, gave $S = 1.3$ at 473 K and was lower than that from Fig. 2 ($S = 1.8$). This difference was considered to be due to σ in Fig. 4a being not completely saturated under oxygen flowing at the rate of $1\,l\,min^{-1}$ for 1 h. For times larger than $t = 1, 3$ and 5 h, σ decreased with increase in t, for $t = 2, 3$, and 6 h, σ decreased with increase in t.

4. Discussion

4.1. Effect of gas atmospheres on conductivity

In Fig. 2, the relationship between σ under argon or oxygen, temperature, T, was fitted to the equation $\sigma\,T = \sigma_0 \exp(-W_a/kT)$ [18, 19] by the least least square technique between 303 and 473 K. In argon gas atmosphere, $r^2 = 0.9985$ (r is the correlation coefficient), and in oxygen gas atmosphere, $r^2 = 0.9985$ was obtained for $R = 1.04 \times 10^{-3}\,S\,cm^{-1}$ (R is the range) in σ, indicating a satisfactory fit. For the present glass it was confirmed that the electrical conduction in argon and oxygen gas atmospheres was due to SPH conduction, as well as in air for the bulk glass [10]. The activation energy for conduction, W_a, calculated from the data between 303 and 473 K in Fig. 2, was $W_a = 0.304$ eV in argon and $W_a = 0.321$ eV in oxygen, respectively. W_a in air was determined to be 0.310 eV. W_a in argon was lower but was higher in oxygen than that in air. The pre-exponential factor, σ_0, was calculated using the data from Fig. 2: values of $\log \sigma_0 = 3.7\,S\,cm^{-1}\,K$ in argon and $\log \sigma_0 = 3.7\,S\,cm^{-1}\,K$ in oxygen were obtained. These values are almost the same as that of $\log \sigma_0$ ($= 4.0\,S\,cm^{-1}$) for V_2O_5–SnO–TeO_2 glasses [10], hence it was confirmed that SPH conduction also holds in argon and oxygen gases, as it does in air.

4.2. Effect of oxygen partial pressure on conductivity

From Fig. 3, it was considered that variations in σ of the glass under different P_{O_2} were due to oxygen adsorption. However, in general, the conductivity change due to gas adsorption occurs very rapidly from less than 1 min [3, 6] to several minutes [5] after introducing the gases. In the present glass, the results in Figs 3 and 4 gave a response time of about 1 h. Therefore, it is appropriate to interpret the results on the basis of diffusion of oxygen into the glass, similar to the case of V_2O_5–SrO–Sb_2O_3 glass [8].

The conduction of vanadate glass (n-type semiconductor) is caused by a valence change of V^{4+} ion to V^{5+}, i.e. $V^{4+} \rightleftharpoons V^{5+} + e'$ [18, 19]. When oxygen diffuses into the glass, it traps conducting electrons, resulting in a gradual increase in V^{5+} ion concentration in the oxygen diffusion layer and, hence, a gradual decrease in conductivity of the sample occurs with time. From this, it is expected that change in σ will be influenced by P_{O_2}. Because Fig. 3 presented variations in σ with P_{O_2}, we can discuss the relationship between σ and P_{O_2}.

Diffusion of oxygen into the glass is possible by dissolution of it in the glass network and the oxygen atom in the glass network, O_O^x, is expressed by [8]

$$O_O^x = V_O^{\cdot} + e' + 1/2O_2 \tag{1}$$

where $1/2O_2$ is the oxygen atom diffused and dissolved in the glass network and $V_O^{\cdot}$ is the oxygen vacancy, then we have

$$[e']\,[V_O^{\cdot}]\,P_{O_2}^{1/2} = K_{V_O^{\cdot}} \tag{2}$$

where $K_{V_O^{\cdot}}$ is the equilibrium constant. Because $[e'] = [V_O^{\cdot}]$, Equation 2 yields

$$[e'] = K_{V_O}^{1/2}\,P_{O_2}^{-1/4} \tag{3}$$

thus

$$\sigma = e\mu[e'] \propto P_{O_2}^{-1/4} \tag{4}$$

where μ is the mobility of electron, e' is the electron charge.

For V_2O_5–SrO–Sb_2O_3 glass [8], Equation 4 in which the saturated values of the conductivity depended on $P_{O_2}^{-1/4}$ was qualitatively explained. In the

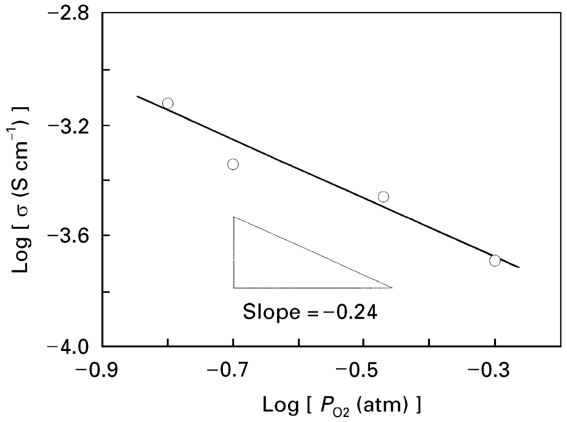

Figure 5. Conductivity of $50V_2O_5 \cdot 20SnO \cdot 30TeO_2$ glass against P_{O_2} at 473 K. The solid line is the regression line calculated by the least square method. ($r^2 = 0.9461$, r = correlation coefficient).

present work, we discuss the results in Fig. 3 quantitatively. Fig. 5 shows the relationship between log σ at 473 K and log P_{O_2}. The saturated σ were taken from the data in Fig. 3 for $t = 1$ h. Although the $50V_2O_5 \cdot 20SnO \cdot 30TeO_2$ glass [10] was previously indicated to be n-type semiconductor, it was confirmed again to be n-type semiconductor because the slope in Fig. 5 was negative. We fitted the data in Fig. 5 to the relationship between log σ and log P_{O_2} by the least square technique, and $r^2 = 0.9461$ (r = correlation coefficient) was obtained. The slope between log σ and log P_{O_2} was -0.24, which agreed satisfactorily with the theoretical slope -0.25. From the above discussion, the variations of σ under mixed gases of oxygen and argon could be explained by the oxygen diffusion and dissolution model. This fact means that μ is hardly influenced by the oxygen diffusion, and the carrier concentration alone is affected.

4.3. Dynamic changes in conductivity

We discuss the relationship between σ in argon or oxygen gas atmosphere and elapsed time, t, using an oxygen diffusion model. The glass sample having a layer containing diffused oxygen can be simply represented by a rectangular sheet with an electrode spacing L, electrode width w, and sample thickness $d (d \ll w)$, and an oxygen-diffusion layer with thickness $X (X \ll d)$ on both sides. Using the bulk glass conductivity, σ_b, and that of the oxygen-diffusion layer, σ_s, the average conductivity, σ, for the present measurement method of resistance is expressed by [29]

$$\sigma = \sigma_b - \Delta\sigma X/d \tag{5}$$

where $\Delta\sigma = \sigma_b - \sigma_s$. When oxygen gas is introduced into the system, the oxygen-diffusion layer increases with elapsed time. Then, the thickness of the larger X measured from the surface to the interior is given by [30]

$$\mathrm{d}X/\mathrm{d}t = CDv_0/X = kX \tag{6}$$

where C is a constant, D the diffusion coefficient for oxygen, and v_0 the volume of an oxygen atom, and $k = CDv_0$. Integration of Equation 6 yields the well-known parabolic increase in X with time t

$$X^2 = 2kt \tag{7}$$

Thus we have, combining Equation 5 with Equation 7

$$\sigma(t) = \sigma_b - \alpha t^{1/2} \tag{8}$$

where $\alpha = \Delta\sigma(2k)^{1/2}/d$.

Next, when the flowing gas is switched from oxygen to argon after the thickness of the oxygen diffusion layer reached $X = X_0$ at $t = t_0$, the diffused oxygen dissolved in the glass diffuses out again from the surface [8]. The relationship between thickness of the oxygen diffused-out layer, X, measured from X_0 to the surface and t, is given by

$$\mathrm{d}(-X)/\mathrm{d}t = k'/(-X) \tag{9}$$

where $k' = C'D'v_0$, where C' is constant and D' is the diffusion coefficient for oxygen when the flowing gas is switched from oxygen to argon. Integration of Equation 9 yields

$$(X - X_0)^2 = 2k'(t - t_0) \tag{10}$$

Combining Equation 5 with Equation 10, we have

$$\sigma = \sigma(t_0) + \beta(t - t_0)^{1/2} \; (t \geqslant t_0) \tag{11}$$

where $\sigma(t_0) = \sigma_b - \Delta\sigma(X_0/d)$ and $\beta = \Delta\sigma[(2k')^{1/2}/d]$. Fig. 4 presents the relationship between experimental log σ and t, together with the theoretical curves (solid lines) calculated using Equations 8 and 11. In Fig. 4, the initial data of σ for $0 < t \leqslant 1$ h includes the effect of the air dissolved previously and diffused out from the glass surface by introducing argon gas. For $1 \text{ h} < t \leqslant 6$ h, satisfactory agreements between the experimental and calculated curves were found. Parameters α and β in Equations 8 and 11, used for the calculation, are given in Table I; $\alpha = (0.835 - 3.938) \times 10^{-4}$ S cm^{-1} h$^{-1/2}$ and $\beta = (0.737 - 2.181) \times 10^{-4}$ S cm^{-1} h$^{-1/2}$ were obtained, for the best fits with the experimental curves. For V_2O_5–SrO–Sb_2O_3 glass [8] $\alpha = (1.3 - 6.6) \times 10^{-3}$ S cm^{-1} h$^{-1/2}$ and $\beta = (0.9 - 4.5) \times 10^{-4}$ S cm^{-1} h$^{-1/2}$, were larger than the values of α and β for the present glass. These differences were due to the term in $\Delta\sigma$ of $\alpha = \Delta\sigma[(2k)^{1/2}/d]$ and $\beta = \Delta\sigma[(2k')^{1/2}/d]$ for the present glass being lower than that for V_2O_5–SrO–Sb_2O_3 glass [8], assuming that k, d in α and k,$'d$ in β were unchanged.

In Table I, α and β decreased with time, t, at each temperature (473, 453 and 433 K). The reason was considered to be that $\Delta\sigma$ decreased with t, resulting in a decrease in α; in contrast, the amount of dissolved oxygen decreased with time by diffusing out from the sample, which resulted in a decrease in β.

In Fig. 4, log σ at $t = 3$ and 5 h was lower than that at $t = 1$ h because the dissolved oxygen was not completely diffused out from the glass surface at $t = 1$ h. So it was considered that for returning to the initial σ, an argon gas flow for more than 1 h was necessary. From the above discussion, the dynamic changes in conductivity were attributed to the oxygen diffusion on exchanging argon for oxygen and the oxygen desorption by rediffusion on exchanging oxygen for

TABLE I Parameters α and β calculated using Equations 8 and 11

Temperture (K)	σ_b (10^{-3} S cm^{-1})	α (10^{-4} S cm^{-1} h$^{-1/2}$)	β (10^{-4} S cm^{-1} h$^{-1/2}$)	α (10^{-4} S cm^{-1} h$^{-1/2}$)	β (10^{-4} S cm^{-1} h$^{-1/2}$)	α (10^{-4} S cm^{-1} h$^{-1/2}$)
473	1.697	3.938	2.181	2.529	2.071	2.495
453	1.109	1.653	1.153	1.545	1.061	1.329
433	0.749	0.990	0.798	0.975	0.737	0.835
Time (h)	0	$1 < t \leqslant 2$	$2 < t \leqslant 3$	$3 < t \leqslant 4$	$4 < t \leqslant 5$	$5 < t \leqslant 6$

argon, and the present vanadium tellurite glass was indicated to have potential applicability to an oxygen gas sensor.

5. Conclusion

The d.c. electrical conductivity and oxygen gas-sensing behaviour for n-type semiconducting V_2O_5–SnO–TeO_2 glass with composition V_2O_5 : SnO : TeO_2 = 50 : 20 : 30 mol % was investigated in argon and oxygen gas atmospheres at temperatures ranging from 303–473 K. σ in argon was higher than σ in oxygen. The experimental relationship between σ and P_{O_2}, could be quantitatively explained by the theoretical $\sigma \propto P_{O_2}^{-1/4}$ relation. Changes in conductivity by switching the flowing gas atmosphere between argon and oxygen were reproducible, and a sensitivity of $S = 1.3$ was obtained under oxygen gas. Good agreements between the theoretical σ–t relation calculated on the basis of the oxygen diffusion model, and the experimental σ–t relationship, were found. The present vanadium tellurite glass was exhibited to possess potential applicability to an oxygen gas sensor.

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