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Review

Perovskite oxides for semiconductor-based gas sensors

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Abstract

The oxygen partial pressure dependence of the point defect concentration, and thus conductivity, in oxide semiconductors allows for their use in high-temperature gas sensors. In addition to responding to oxygen partial pressure, the resistance of oxide semiconductors can be affected by other gases, such as carbon monoxide, hydrocarbons and ethanol, which creates opportunities for developing new sensors, but also leads to interference problems. The most common oxide used in such sensors is tin oxide, although other simple oxides, and some mixed oxides, are also used. The focus of this paper is on the use of perovskite oxides in semiconductor-based gas sensors. The perovskite structure, with two differently-sized cations, is amenable to a variety of dopant additions. This flexibility allows for control of the transport and catalytic properties, which are important for improving sensor performance.

Keywords: Resistance-based gas sensors; Strontium titanate; Oxygen sensors

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1. Introduction

In response to the need for measuring gas concentrations to provide feedback control and to monitor emissions in combustion processes, gas sensors have been developed using a variety of approaches [1–7]. High-temperature sensors for use directly in the combustion environment are often based on ionic conductors. Pure ionic conductors are used in potentiometric, mixed-potential or amperometric sensors [8–12], but mixed (ionic–electronic) conductors are used in semiconductor-based sensors [13–16]. The response of semiconductor-based

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sensors is generated by the equilibration of oxygen in the gas phase with ionic and electronic point defects in the oxide semiconductor. The oxide most commonly used in such sensors is SnO_2, but other oxides, such as TiO_2 and WO_3, are also used. The focus of this paper is on the use of perovskite oxides in semiconductor-based gas sensors. The perovskite structure forms from a wide variety of oxides with transport properties ranging from predominantly ionic conduction to predominantly electronic conduction. Perovskite oxides are particularly attractive for high-temperature applications, because, in addition to often having high melting and/or decomposition temperatures, they can provide microstructural and morphological stability to improve reliability and long-term sensor performance. In addition, the perovskite structure has two differently-sized cations, which makes it amenable to a variety of dopant additions. This doping flexibility allows for control of the transport and catalytic properties to optimize sensor performance for particular applications.

2. Oxygen sensors

2.1. $SrTiO_3$

2.1.1. Point defects

The perovskite oxide most commonly used in oxygen sensors is $SrTiO_3$, the intrinsic ionic point defects in which are strontium and oxygen vacancies (i.e. Shottky defects) [17–19]. Thus, at low oxygen partial pressures, the predominant point defects are oxygen vacancies and electrons, which form by Eq. (1),

$$O_O^x = \tfrac{1}{2}O_2 + 2e' + V_O^{\bullet\bullet} \quad (1)$$

the equilibrium of which is described by Eq. (2):

$$K_I = \frac{p_{O_2}^{1/2} n^2 [V_O^{\bullet\bullet}]}{[O_O^x]} \quad (2)$$

If the predominant point defects are oxygen vacancies and electrons, charge neutrality requires that

$$2[V_O^{\bullet\bullet}] \approx n \quad (3)$$

which, when used in Eq. (2) along with unit activity of oxygen ions on oxygen sites ($[O_O^x] = 1$), results in the following expression

$$n = (2K_I)^{1/3} p_{O_2}^{-1/6} \quad (4)$$

for the oxygen partial pressure dependence of the electron concentration, and thus the conductivity.

At high oxygen partial pressures, the predominant point defects are strontium vacancies and holes, which can form by oxygen occupying a vacant SrO unit on the surface according to Eq. (5),

$$\tfrac{1}{2}O_2 + \{V_{Sr}'' + V_O^{\bullet\bullet}\} = V_{Sr}'' + O_O^x + 2h^\bullet \quad (5)$$

or by removing a strontium ion to form a separate SrO phase according to Eq. (6):

$$\tfrac{1}{2}O_2 + Sr_{Sr}^x = V_{Sr}'' + 2h^\bullet + SrO \quad (6)$$

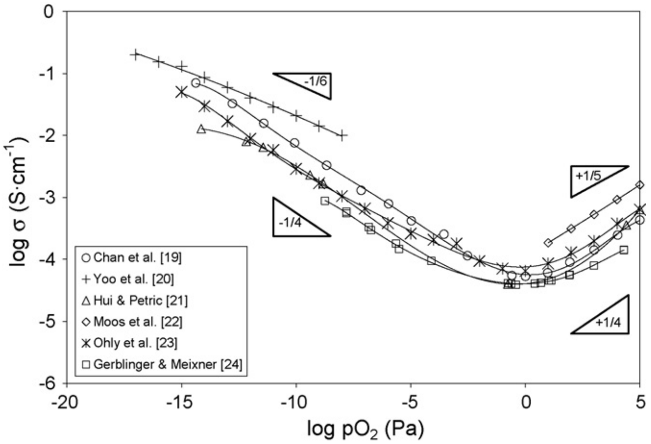

Fig. 1. Conductivity of undoped $SrTiO_3$ at 800 °C [19–24].

Either of these reactions, when combined with the charge neutrality requirement,

$$2[V_{Sr}''] \approx p \quad (7)$$

result in the same oxygen partial pressure dependence for the electronic conductivity as given by Eq. (8):

$$p = (2K_{II})^{1/3} p_{O_2}^{1/6} \quad (8)$$

Fig. 1 [19–24] shows that the oxygen partial pressure dependence of the conductivity of undoped $SrTiO_3$ contains both n-type and p-type regimes. At very low oxygen partial pressures, the oxygen partial pressure dependence is close to that predicted by Eq. (4). However, with increasing oxygen partial pressure, the slope increases and is closer to −1/4 than −1/6. Similarly, the slope in the p-type regime is typically in the range of 1/5 to 1/4, which is larger than that predicted by Eq. (8).

This deviation of the observed oxygen partial pressure dependence of the electronic conductivity from that expected for intrinsic Shottky defects has been attributed to the presence of additional ionic defects [19]. One possibility is that the Sr/Ti ratio in the perovskite is less than one, which would result in the formation of excess strontium vacancies. The strontium-deficient composition can result from the removal of strontium to form SrO (Eq. (6)) or a strontium-rich Ruddlesden–Popper phase [25]. The other possibility is that, even in nominally undoped $SrTiO_3$, impurities are present in amounts large enough to establish the point defect concentration. Using aluminum as an example of an acceptor dopant, Al_2O_3 would replace TiO_2 according to Eq. (9),

$$Al_2O_3(-2TiO_2) = 2Al_{Ti}' + 3O_O^x + V_O^{\bullet\bullet} \quad (9)$$

which would create oxygen vacancies. If the concentration of oxygen vacancies is fixed by the dopant level and the nonstoichiometry (Sr/Ti ratio), the charge balance is given by Eq. (10):

$$[V_O^{\bullet\bullet}] \approx [V_{Sr}''] + \tfrac{1}{2}[Al_{Ti}'] \quad (10)$$