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Temperature-independent resistive oxygen sensors based on $SrTi_{1-x}Fe_xO_{3-\delta}$ solid solutions

Avner Rothschild [a,*], Scott J. Litzelman [a], Harry L. Tuller [a],
Wolfgang Menesklou [b], Thomas Schneider [b], Ellen Ivers-Tiffée [b]

[a] *Department of Materials Science and Engineering, MIT, Cambridge, MA 02139, USA*
[b] *Institut für Werkstoffe der Electrotechnik, Universität Karlsruhe (TH), 76131 Karlsruhe, Germany*

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Abstract

$SrTi_{0.65}Fe_{0.35}O_{3-\delta}$ (STF35) is a potential candidate for oxygen sensors in lean burn engines due to its strong sensitivity to oxygen partial pressure variations and negligible cross-sensitivity to temperature fluctuations. To understand the origin of this unique phenomenon, the temperature coefficient of resistance (TCR) of $SrTi_{1-x}Fe_xO_{3-\delta}$ (STF) solid solutions with varying compositions between $SrTiO_3$ and $SrFeO_{3-\delta}$ was systematically analyzed. Changes in TCR from negative values at low to positive values at high iron concentrations were found to be correlated to systematically decreasing bandgap energy with increasing Fe/Ti ratio. At an intermediate composition of $x = 0.35$ (STF35), the bandgap energy is such that the Fermi energy lies just far enough above the valence band to compensate for the temperature-dependence of the mobility, yielding a zero TCR from the product of the free carrier (holes) concentration and mobility terms. We propose that the variations in the bandgap energy of STF solid solutions are due to additional bands derived largely from Fe^{3+}/Fe^{4+} and Fe^{2+}/Fe^{3+} states. These bands lie between the O 2p valence and Ti 3d conduction bands of $SrTiO_3$, and due to variations in their position and width, the bandgap energy of STF solid solutions decreases with increasing iron concentration.

Keywords: Oxygen sensors; Temperature coefficient of resistance (TCR); Fe-doped $SrTiO_3$; $SrTi_{1-x}Fe_xO_{3-\delta}$

1. Introduction

Oxygen sensors are widely used in automotive exhaust gas control systems for optimization of fuel combustion and conversion of deleterious combustion products such as CO, hydrocarbons, and NO_x to safer gases such as CO_2, H_2O, and N_2 by way of the three way catalyst [1]. The oxygen sensor market is dominated by electrochemical ZrO_2-based sensors [2]. The more common potentiometric sensor has a simple and robust design but is effective only over a narrow range bordering the stoichiometric air/fuel ratio where there are large variations in oxygen partial pressure. Amperometric oxygen sensors extend operation to lean conditions, but their design is considerably more complex [1,2].

Possible alternatives to ZrO_2-based oxygen sensors are resistive-type sensors based on semiconducting oxides such as TiO_2 [3]. These sensors are sensitive to oxygen pressure and have a relatively simple design. However, their response is typically complicated by cross-sensitivity to temperature. Efforts have thus been directed towards finding materials with temperature-independent oxygen pressure sensitivity [4]. $SrTi_{1-x}Fe_xO_{3-\delta}$ (STF) solid solutions were found to shift their temperature coefficient of resistance (TCR) from negative to positive as iron increasingly substitutes for titanium, with the TCR tending towards zero at $x = 0.35$ [5]. This material, $SrTi_{0.65}Fe_{0.35}O_{3-\delta}$ (STF35), thus becomes a prospective oxygen sensor candidate for automotive applications.

The origin of the temperature-independent conductivity of these sensors was attributed to offsetting contributions from the intrinsic electron-hole generation, which tends to increase the conductivity as the temperature increases, and

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[*] Corresponding author. Tel.: +1 617 253 2364.
E-mail address: avner@mit.edu (A. Rothschild).

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the reduction reaction which decreases the (p-type) conductivity at relatively high oxygen pressures [1,4,5]. Based on this idea, Menesklou et al. [5] proposed that the bandgap energy (E_g) of STF solid solutions varies as a function of the Fe/Ti ratio such that at an iron content of 35% (STF35) the bandgap energy and the reduction enthalpy (ΔH_{red}) balance one another to give a zero activation energy (E_A), i.e. $E_A = E_g - \Delta H_{red}/2 = 0$. However, the contribution of the mobility term to the TCR was not taken into account in that paper, and the authors did not provide an insight into the source of the variation in the bandgap energy as a function of composition. In this work, we investigate the TCR behavior of STF solid solutions in more details. Starting from the general expression for the conductivity for these p-type oxides (at high oxygen pressures), we derive the conditions for zero TCR. In order to obtain zero TCR, the temperature-dependencies of the hole mobility and concentration should balance one another, since the former, in general, has a positive contribution to the TCR whereas the latter has a negative one. This requires the mobility to have a rather strong temperature-dependence and the Fermi energy (E_F) to lie close (within a few tenths of an eV) to the valence band. Due to ionic compensation of acceptor-like Fe substitutionals by donor-like oxygen vacancies, increasing the iron concentration has a negligible net effect on the absolute position of the Fermi energy. A reduction in the distance between the Fermi energy and the valence band is achieved in STF solid solutions instead by narrowing the effective bandgap energy with increasing iron concentrations. By analyzing conductivity measurements as a function of oxygen pressure and temperature for different STF solid solutions, we show that the bandgap energy changes as a function of the iron content (x) as $E_g(x) = 3.26 - 1.93x + 0.54x^2$ eV. Therefore, at intermediate iron concentrations around $x = 0.35$ the Fermi energy lies just at the right distance above the valence band such that the temperature-dependence of the hole concentration is exactly balanced by that of the hole mobility to give zero TCR. At lower iron concentrations ($x < 0.35$), the contribution of the carrier concentration prevails and the TCR is therefore negative, while at higher concentrations ($x > 0.35$), the mobility prevails and the TCR is positive.

2. Theoretical background

Under lean burn conditions, STF solid solutions exhibit p-type semiconductivity in which the electrical conductivity (σ) dependence on oxygen pressure ($p(O_2)$) typically follows a $\sigma \propto p(O_2)^{+1/4}$ dependence [5]. The general expression for the electrical conductivity is $\sigma = q\mu p$, where q is the elementary charge, μ is the hole mobility, and p the hole concentration. It should be noted that both μ and p are temperature-dependent and one should take account of the temperature-dependencies of both of these terms when analyzing the TCR. The mobility has a typical power law temperature-dependence that can be written $\mu = \mu_0 T^{-m}$, where μ_0 is a constant, T is the temperature, and m is the power exponent. For crystalline semiconductors with low (<1%) defect concentration $m = 1.5$ at high temperatures due to scattering by phonons [6], but m may be considerably larger (e.g., $m = 4.5$ [7]) in disordered semiconductors due to charge localization and other disorder effects. The carrier concentration has a typical Arrhenius-type temperature-dependence, $p = N_V \exp(-E_F/kT)$ (taking the valence band edge as the origin of the energy scale, i.e. $E_V = 0$), where N_V is the effective density of states in the valence b and and k is the Boltzmann constant. It should be noted that N_V is temperature-dependent, $N_V = 2(2\pi m_p{}^* kT/h^2)^{1.5}$, where $m_p{}^*$ is the hole effective mass and h is Planck's constant [6]. Therefore, the temperature-dependence of the electrical conductivity is

$$\sigma = \sigma_0 T^{(1.5-m)} \exp\left(-\frac{E_F}{kT}\right), \tag{1}$$

where σ_0 is a constant ($\sigma_0 = 2q\mu_0(2\pi m_p{}^* k/h^2)^{1.5}$).

Due to the redox reaction, $O_o^x \leftrightarrow \frac{1}{2}O_{2(g)} + V_o^{\bullet\bullet} + 2e'$, in which a metal-oxide exchanges lattice oxygen with the ambient gas atmosphere, the electrochemical potential of electrons is coupled to that of the oxygen gas. Consequently, the Fermi energy varies with the logarithm of the oxygen pressure [8]

$$E_F = E_{F,0} - \left(\frac{kT}{4}\right) \ln\left[\frac{p(O_2)}{p(O_2)_0}\right], \tag{2}$$

where $E_{F,0}$ is the Fermi energy at a reference oxygen pressure $p(O_2)_0$. Substituting Eq. (2) into Eq. (1) yields

$$\sigma = \sigma_0 T^{(1.5-m)} \exp\left(-\frac{E_{F,0}}{kT}\right)\left[\frac{p(O_2)}{p(O_2)_0}\right]^{+1/4}. \tag{3}$$

Eq. (3) gives the temperature and oxygen pressure dependencies of the conductivity of semiconducting metal-oxides in the p-type regime at high oxygen pressures. A similar relationship can be also derived for the conductivity in the n-type regime at low pressures, with a power exponent of −1/4 (instead of +1/4) for the oxygen pressure.

Using relation (3), one can calculate the condition for zero TCR ($d\sigma/dT = 0$), which gives the temperature T_0 at which the TCR is zero at the reference oxygen pressure $p(O_2)_0$:

$$T_0|_{p(O_2)_0} = \frac{E_{F,0}}{k(m-1.5)}. \tag{4}$$

In principal, any semiconducting metal-oxide that satisfies the above relationship between $E_{F,0}$ and m will exhibit a zero TCR at temperature T_0 and oxygen pressure $p(O_2)_0$. However, in practice most metal-oxides have too high a Fermi energy or too small a power exponent (m) such that this condition is only satisfied at very high temperatures or pressures. For instance, with $m = 1.5$, typical for semiconductors with mobilities dominated by phonon scattering [6], the Fermi energy should lie at the valence band edge ($E_F = 0$), or in other words the semiconductor should be degenerate, in order to have zero TCR at finite temperatures. Potential candidates for temperature-independent oxygen sensors in automotive