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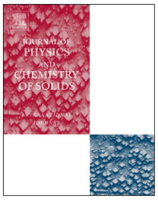

Theory of oxidation/reduction-induced valence transformations of metal ion dopants in oxide crystals mediated by oxide-vacancy diffusion: I. Thermodynamic analysis

M. Sinder*, Z. Burshtein, J. Pelleg

Materials Engineering Department, Ben-Gurion University of the Negev, P.O. Box 653, Beer-Sheva 84105, Israel

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ABSTRACT

We consider theoretically valence transformations of doping metal ions in oxide crystals induced by oxidation and reduction obtained by changes in the ambient oxygen partial pressure. Three types of oxygen vacancies are assumed to mediate transformations: neutral, singly ionized, and doubly ionized. We provide thermodynamic equilibrium analyses, yielding concentration relations among the oxygen vacancy, metal ions, holes and electrons as functions of the ambient oxygen pressure. The results suggest that experimental study of different species concentrations at thermodynamic equilibrium as functions of pressure and temperature should allow assessment of various reversible reaction constants controlling the process. In the Part II companion paper, the kinetic (diffusion) characteristics are considered in detail.

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1. Introduction

Oxide crystals are commonly used as hosts for different metal ions, for example as laser gain materials, or light saturable absorbers [1]. At elevated temperatures, the crystal may loose lattice oxygen when exposed to an ambient reducing atmosphere, thus creating oxide vacancies, and possibly free electrons and holes, overall maintaining an average electro-neutrality. Oxygen diffusion in oxide crystal is of interest in relation to color centers related to the oxygen vacancies [2], as well as an agent for valence transformation of embedded metal ions (dopants) [3]. These processes belong to the general subject of chemical diffusion in solids, which is of considerable theoretical and practical importance [4–7].

We consider the issue in two companion papers; the present one, Part I, provides a thermodynamic analysis, namely the concentration of the various species involved in the physical and chemical processes after achievement of thermodynamic equilibrium. From an experimental point of view it relates to very small rates of the ambient oxygen pressure changes. The second one, Part II, will address the kinetic aspects, namely the temporal changes and spatial profiles developing during the oxygen vacancy diffusion upon sudden changes in the ambient oxygen pressure.

In the present work we have considered three types of oxygen vacancies, depending on the ionization state: a neutral vacancy, and a single or a double ionized one. The dopant metal M may exist in the matrix in only two ionization states: p-times ionized M^{p+} in the unreduced matrix, or $(p-1)$ times ionized $M^{(p-1)+}$ after accepting an electron following reduction. Oxidation and reduction processes of the metal ions are thus indirectly induced by changes in the ambient partial oxygen pressure.

Such features allow for experimental assessment of different process parameters by measuring the metal ion concentrations during oxidation and reduction.

2. Model

Our model considers a crystal oxide matrix where dopant metal ions (M-dopant, hereafter) replace lattice metal ions of the same $p+$ ionic state. The M-dopant is assumed to be immobile, yet susceptible to changes of its valence state. During reduction, free oxygen molecules $(1/2)O_2$ removed from the solid get into the ambient gas phase (e.g., by heating the sample in vacuum). Oxygen vacancies are thus created at the crystal surface, and then diffuse into the bulk. During oxidation, the process is reversed. Since lattice oxygen exists as a double-negative ion, the evaporation of a neutral atom leaves behind a free lattice site, plus two electrons. A crucial point in the oxidation/reduction mechanisms is the vacancy charge state, namely the fate of the two said electrons. Three options may be considered (see p. 41, Table 22.2 in Ref. [4]): in the first, the two electrons remain bound to the vacant O^{2-} lattice site, thus forming a V_O^{2-}-type vacancy. This is an electrical neutral species relative to the parent lattice. In the second option, one electron turns free or gets trapped, the other electron remains bound to the vacant lattice site to form a V_O^{-}-type vacancy. In the

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* Corresponding author.
E-mail address: micha@bgu.ac.il (M. Sinder).

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third option, both electrons turn free or get trapped, and the vacant lattice site remains bare $-V_O^0$.

Important issues to address are the energy depth of the M-dopant, and the conductivity type of the "virgin" crystal, namely the one without the M-dopant, and devoid of vacancies. Had the dopant been a shallow acceptor under thermal equilibrium conditions, only a small fraction of the M-dopant ions may exist as M^{p+}; most will turn into $M^{(p-1)+}$ ones. Introduction of oxygen vacancies (reduction) will thus have no effect on the M-dopant state. Thus in our model, the M-dopant M^{p+} state will be assumed to reside close to the matrix mid energy-gap.

Codoping the crystal with donor impurities will also change the M-dopant state into $M^{(p-1)+}$, thus rendering entirely ineffective the said valence transformation by introduction of oxygen vacancies. Furthermore, codoping with shallow acceptors will make them competitors to the M-dopant valence transformation. Initial reduction will act to compensate the p-type characteristics of the sample, and only afterwards, M-dopant valence transformations may become apparent. In our model we limit ourselves to consider only the case of an intrinsic host crystal, namely a crystal devoid of any donors or acceptors.

In Fig. 1 we show two energy scheme options for the energy states of the M-dopant and vacancy in the oxide crystal. The M^{p+} energy lies close to the mid-gap, yet to emphasize its role as an acceptor under reduction, it is placed slightly below the mid-gap. The V_O^{2-} energy always lies above that of M^{p+} to indicate its role as a donor under reduction. In Fig. 1(a), it is assumed to be shallow, with depth of the order of the free electronic polaron, while in Fig. 1(b) it is assumed to lie deep below the conduction band.

Oxygen evaporation at the surface is described by either of three chemical reactions:

$$O^{2-}(\text{solid}) \leftrightarrow \tfrac{1}{2}O_2(\text{gas}) + V_O^{m-2} + me^-, \tag{1}$$

where e^- indicates a free electron (in fact a free electronic polaron), while the said three chemical reactions relate to the $m = 0,\ 1,\ 2$ cases. The presence of free electrons must be accounted for against the presence of free holes (free hole polarons) by

$$e^- + h^+ \leftrightarrow 0. \tag{2}$$

By assumption, the metallic dopant ion M^{p+} is a deep acceptor; namely, under proper conditions it may accept an additional electron and change into an $M^{(p-1)+}$. For the shallow oxygen vacancy case (Fig. 1(a)), free electrons are present, and the M-dopant may trap a free electron by the reaction

$$M^{p+} + e^- \leftrightarrow M^{(p-1)+}. \tag{3}$$

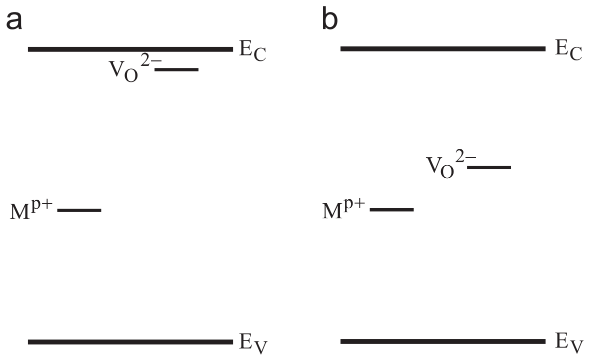

Fig. 1. Energy scheme for oxide crystal, M-dopant and oxygen vacancy V_O^{2-} considered in our analysis. (a) Vacancy V_O^{2-} below, yet close to the rigid lattice conduction band, depth being of the order of the electronic polaron binding energy. (b) Vacancy V_O^{2-} deep below the rigid lattice conduction band. In both cases, the V_O^{2-} energy is higher than that of M^{p+}.

Table 1
Translation of species′ nomenclature used in our present paper to the Kröger–Vink notation. The subscript *Me* is used to indicate the lattice metal of the oxide matrix that may be replaced by the dopant metal M.

"Optical" nomenclature	V_O^{2-}	V_O^-	V_O^0	h^+	e^-	M^{p+}	$M^{(p-1)+}$
Kröger–Vink notation	$V_O^\times$	$V_O^\bullet$	$V_O^{\bullet\bullet}$	$h^\bullet$	e'	$M_{Me}^\times$	M'_{Me}

For the deep oxygen vacancy case (Fig. 1(b)), virtually no free electrons exist, namely $m = 0$, but the M-dopant may receive an additional electron from a nearby neutral oxygen vacancy, whose energy is assumed to be higher. The reaction for this special case may be written as

$$M^{p+} + V_O^{2-} \leftrightarrow \{M^{(p-1)+}V_O^-\}. \tag{4}$$

An assumption inherent of Eq. (4) is that the $M^{(p-1)+}$ ion and the ionized oxygen vacancy V_O^- form an immobile complex $\{M^{(p-1)+}V_O^-\}$.

Notably, in the present paper we adhere to a nomenclature practiced in optical studies of doped materials. An alternative (and complementary) nomenclature is the Kröger–Vink notation mostly practiced by solid-state chemists. For the benefit of readers belonging to the latter scientific community, in Table 1 we provide a translation of all above species′ nomenclature to the Kröger–Vink notation.

3. Thermodynamic analysis

Applying the law of mass action to Eqs. (1)–(4) yields

$$\frac{P^{1/2}[V_O^{m-2}][e^-]^m}{[O^{2-}]} = K_{1,m}, \tag{5}$$

$$[e^-][h^+] = K_2, \tag{6}$$

$$\frac{[M^{p+}][e^-]}{[M^{(p-1)+}]} = K_3, \tag{7}$$

$$\frac{[M^{p+}][V_O^{2-}]}{[\{M^{(p-1)+}V_O^-\}]} = K_4, \tag{8}$$

where P is the gas oxygen partial pressure, and $K_{1,m} \cdots K_4$ are the temperature-dependent equilibrium reaction constants for the reactions described by Eqs. (1)–(4), respectively [4, vol.2, pp. 73–76; 167–171].

In our analysis we consider separately two different cases: the $m = 0$ case related to Fig. 1(b), and the $m = 1, 2$ case related to Fig. 1(a).

3.1. The neutral vacancy case ($m = 0$)

In the $m = 0$ case, Eq. (5) reduces to

$$\frac{P^{1/2}[V_O^{2-}]}{[O^{2-}]} = K_{1,0}\,. \tag{9}$$

Then

$$[V_O^{2-}] = [O^{2-}]\frac{K_{1,0}}{\sqrt{P}}\,. \tag{10}$$

Under ordinary experimental conditions, the concentration of oxygen vacancies $[V_O^{2-}]$ always remains extremely small compared to that of the lattice oxygen; thus $[O^{2-}]$ may be assumed constant throughout. This in fact requires the use of a sufficiently high partial oxygen pressure: $P \gg K_{1,0}^2$.

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