JOURNAL OF MATERIALS SCIENCE 19 (1984) 1991–1996

Use of thermionic emission for studying of point defects in NiO single crystals

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The thermionic emission method has been used to study atomic point defects in NiO single crystals in the temperature range of 500 to 900 K and oxygen pressure range of 5×10^{-2} to 5×10^{1} Pa. The $P_{O_2}^{1/n}$ dependence of the thermionic emission has been observed and the n parameter increased from 4.25 to 4.80 with increasing temperature in the range of 500 to 900 K. The activation enthalpy of thermionic emission increased slightly from 1.0 to 1.2 eV with decreasing oxygen partial pressure in the range of 5×10^{1} to 5×10^{-2} Pa. This behaviour can be explained by the presence, in NiO single crystals under the above conditions, of the predominant singly ionized nickel vacancies and a small amount of the double ionized nickel vacancies with somewhat different energies of formation.

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1. Introduction

The transition metal monoxides have received much attention due to their importance as model semiconductors and catalysts. The physicochemical properties of transition metal oxides are mainly related to their deviations from stoichiometry. These deviations themselves depend on two important parameters: the temperature and the partial pressure of oxygen in equilibrium with the oxide.

Nickel oxide NiO seems to be one of the transition metal monoxides which have been the subject of numerous studies. It appears from existing results that the predominant defects in this oxide is the nickel vacancy, electrically compensated by electronic holes, which confers to this oxide the properties of a p-type semiconductor.

According to the Kroger–Vink [1, 2] notation, the formation of a nickel vacancy can be written by the formula

$$\tfrac{1}{2}O_2 = O_O + V_{\mathrm{Ni}}^{\alpha} + \alpha h^{\cdot} \qquad (1)$$

where O_O, V_{Ni}^{α} and $h^{\cdot}$ represent, respectively, an oxygen atom on its normal lattice site, an α times ionized nickel vacancy and an electron hole.

With the assumption that V_{Ni}^{α} is the predominant defect in the lattice, the simplified condition for the electrical neutrality can be written as

$$p = \alpha[V_{\mathrm{Ni}}^{\alpha}] \qquad (2)$$

where p is the molar fraction of electron holes $h^{\cdot}$ and $[V_{\mathrm{Ni}}^{\alpha}]$ is the molar fraction of nickel vacancies which is equal to the deviation from stoichiometry. The physicochemical properties of a NiO single crystal are therefore strongly dependent on the nature, the degree of ionization and the concentration of the predominant defects.

Taking into account the electroneutrality condition [2] the equilibrium constant for the formation of nickel vacancies can be written as

$$K_\alpha = \frac{1}{\alpha}\frac{p^{\alpha+1}}{P_{O_2}^{1/2}} \qquad (3)$$

Consequently the carrier concentration can be expressed by the relation

$$p = A \exp\left[-\frac{\Delta H_\alpha^0}{(\alpha+1)RT}\right] P_{O_2}^{1/2(\alpha+1)} \qquad (4)$$

where ΔH_α^0 is the enthalpy of formation of the considered defects. It can be easily noted that the carrier concentration in oxide is a function of the temperature T and oxygen partial pressure P_{O_2} in the equilibrium with the oxide.

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In the investigations of the nature and the degree of the ionization of nickel vacancies in NiO single crystals only electrical conductivity [3–17] trace diffusion [18–22] and thermogravimetric methods [2, 23] were used. Some disagreement still exists concerning many problems related to the properties of nickel vacancies in a NiO single crystal and particularly the degree of the ionization of the cation vacancies remains a subject of discussion. Some authors [4, 6, 9] have determined that the state of ionization of nickel vacancies which can be expressed by $n = 2(\alpha + 1)$ was $n = 4$ and proposed that the predominant defects are singly ionized nickel vacancies. Other [3, 5, 8, 10–12, 15] found that $n = 6$ and consequently explain their results assuming that doubly ionized nickel vacancies are the predominant defects. The occurrence of both types of vacancies has also been suggested in some other studies [7, 13, 16, 17, 21–23]. All these investigations were concentrated essentially at high P_{O_2} above 1 Pa and high temperatures above 1000 K. Investigations by other suitable experimental methods, in particular at low pressure P_{O_2} below 1 Pa and low temperatures below 1000 K, also seem to be interesting. In the last few years the thermionic emission method appeared very useful in the studies of the atomic point defects in the ionic crystals especially in refractory oxides [24–30].

The purpose of this paper is to present the preliminary results of the investigations of the atomic point defects in single crystalline NiO by means of a thermionic emission method. Madjid and Martinez [31] definitely performed the first thermionic emission investigations on NiO single crystal but only the fundamental thermionic emission parameters, i.e. true work function, A, a constant and normal energy distribution of thermoelectrons for a near stoichiometric (1 2 5) NiO single crystal surface have been determined. The obtained results showed moreover that the Fermi level E_F in NiO is rather insensitive to temperature from room to incandescent temperature and that the emission probably originates from the itinerant 4*s* band.

In the present paper after briefly summarizing several theoretical aspects relative to the possibility of the thermionic emission method on the study of the atomic point defects in oxides and after briefly describing experimental details, some preliminary results of the investigations of the atomic point defects in NiO single crystal, being in thermal equilibrium with oxygen in gas phase within the temperature range of 500 to 900 K and within the oxygen pressure range of 5×10^{-2} to 5×10^{1} Pa, have been presented.

2. Theoretical background

First, let us summarize briefly several theoretical aspects that will be used later on. The density of emitted current J_0 (at zero electrical field) at the temperature T is given by the well-known Richardson–Dushman law

$$J_0 = A_0 T^2 (1 - \bar{r}) \exp\left(-\frac{\phi}{kT}\right) \tag{5}$$

where $A_0 = (4\pi mek^2)/h^3 = 120\ \text{Acm}^{-2}\ \text{K}^{-2}$, where m is the mass of free electron, $\bar{r}$ is the mean thermoelectron reflectance coefficient (it will be neglected (at least its variation with P_{O_2})), ϕ is the work function, i.e. the work which must be done to move the electron at the Fermii level E_F from solid to infinity in vacuum.

For a nondegenerate semiconductor Equation 5 take the form

$$J_0 = BnT^2 \exp - \frac{\chi}{kT} \tag{6}$$

where n is the concentration of electrons in the conduction band, χ is the electron affinity, i.e. $\chi = \phi - (E_c - E_F)$, B is a constant in which the effective mass of electrons is a parameter.

Assuming that the electron concentration in the conduction band n is proportional to the concentration of the nickel vacancies V_{Ni}^{α} and then to the hole concentration p in the crystal the density of the emitted current J_0 (at zero electrical field) from the oxide at the given temperature T can be expressed by the equation

$$J_0 = \text{Constant} \times \exp\left[-\frac{\frac{2}{n}\Delta H_{\alpha}^{0}}{RT}\right] P_{O_2}^{1/n} \tag{7}$$

This equation appears to be very useful in the determination of the degree of the ionization α and the enthalpy of the formation ΔH_{α}^{0} of the considered defects in NiO single crystal being in thermal equilibrium with oxygen in the gas phase.

3. Experimental procedure

Experiments were conducted in an UHV stainless steel chamber pumped by means of three zeolite-sorption pumps, titanium sublimation pump with nitrogen cooling and ion sorption pump PZK-100. The oil-free UHV of about 10^{-7} Pa was achieved after bakeout [32]. The system was pumped continuously to produce a perfectly stable adjustable pressure.

Thermionic emission measurements were performed on a nearly stoichiometric green-black NiO single crystal wafer with inorganic impurity concentrations below 10^{-3} % [14] and dimensions of 8 mm x 5 mm x 2 mm. It was polished with diamond paste, degreased in methanol and rinsed in deionized water. The measurements were performed in a planar diode [33]. The NiO single crystal wafer was used as a cathode whereas the semitransparent metal grid was used as an anode. The electron emission was measured in the anode by means of the vibrating electrometer VAJ-51 with current noise below 10^{-15} A. The emitter was indirectly heated and its temperature was monitored by means of iron–constantan thermocouple. In order to obtain the density of the emitted current, J_0, the electron emission was measured as a function of the applied potential V and J_0 was determined by graphical extrapolation to zero cathode–anode voltage of the Schottky curves ($\log J - V^{1/2}$) which are straight lines for a homogenous surface [33].

The pure O_2 gas obtained by thermal decomposition of CuO [34] was introduced to the UHV chamber by means of the metal UHV leak valve ZD-2W. Before the thermionic emission study, the NiO single crystal wafer was annealed for 30 min at 500 K in UHV 10^{-6} Pa and then annealed for 2 h in an oxygen atmosphere at 50 Pa. This procedure causes almost perfect removal of physically adsorbed oxygen and water vapour [32] and homogenous distribution of the defects in NiO single crystal. After the above standardization, the sample was studied by the thermionic emission method within the temperature range 500 to 900 K and oxygen partial pressure within the range of 5 x 10^{-2} to 5 x 10^{1} Pa.

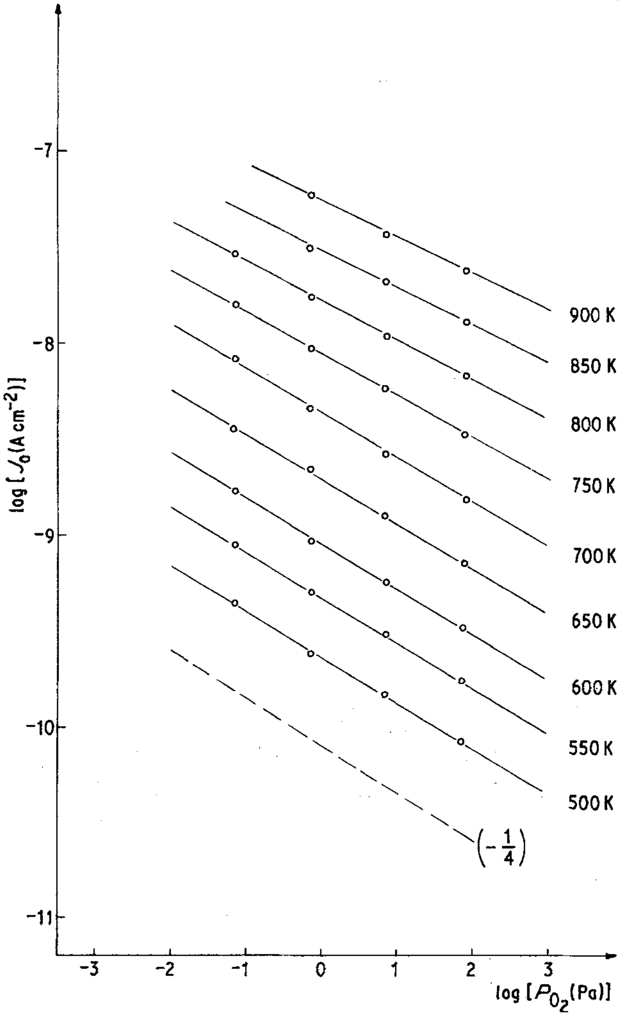

Figure 1 Thermionic emission isotherms of NiO single crystal in thermal equilibrium with oxygen gas phase.

4. Results and discussion

The main results of the investigations are presented in Figs. 1 and 2.

Fig. 1 presents the system of the thermionic emission isotherms of the NiO single crystal in the given oxygen partial pressure P_{O_2} range. As can be seen from Fig. 1 the logarithm of J_0 varies linearly with $\log P_{O_2}$ and can be described by

$$\log J_0 = \text{Constant} + n \log P_{O_2} \qquad (8)$$

TABLE I State of ionization of the nickel vacancies in NiO single crystal in thermal equilibrium with oxygen gas phase in the pressure range of 5×10^{-2} to 5×10^{1} Pa within the chosen temperature range

Temperature of thermal equilibrium, T (K)	State of ionization of nickel vacancies, n
500	4.25
550	4.25
600	4.30
650	4.35
700	4.40
750	4.50
800	4.60
850	4.70
900	4.80

The n parameter, which described the state of ionization of the nickel vacancy for the all annealing temperature, is summarized in Table I. As can be seen from Table I the n parameter increased slightly from 4.25 to 4.80 with increasing annealing temperature of the NiO single crystal in the range 500 to 900 K. Its values indicate that in these technological conditions the predominant defects are singly-ionized nickel vacancies although a small amount of the double-ionized nickel vacancies can also exist. Taking into account the somewhat different experimental conditions and particular oxide purity the obtained n values are in good agreement with those obtained by other authors by electrical conductivity [4, 6, 7, 13] and trace diffusion investigations [20, 22] in nearly the same technological conditions.

The decrease in the thermionic emission current with increasing oxygen partial pressure P_{O_2} at constant temperature may probably be caused by the chemisorption of the oxygen ions in the crystal lattice leading to the increase of the work function observed independently by Dereń and co-workers [35] using a contact potential difference method.

Fig. 2 presents the system of the thermionic emission isobars of NiO single crystal in the given temperature range. As can be seen from Fig. 2 the logarithm of J_0 varies linearly with $1/T$ for the all

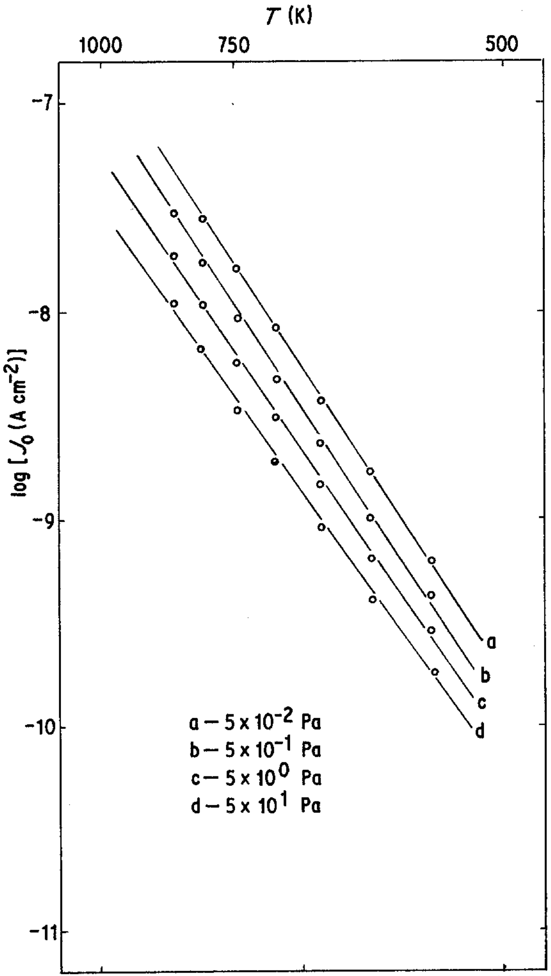

Figure 2 Thermionic emission isobars of NiO single crystal in thermal equilibrium with oxygen gas phase.

TABLE II Enthalpy of formation of the nickel vacancies in NiO single crystal in thermal equilibrium with oxygen gas phase in the temperature range of 500 to 900 K within the chosen oxygen partial pressure range

Oxygen partial pressure, P_{O_2} (Pa)	Enthalpy of formation of nickel vacancies, ΔH^0_α (eV)
5×10^{1}	1.00 ± 0.05
5×10^{0}	1.05 ± 0.05
5×10^{-1}	1.10 ± 0.05
5×10^{-2}	1.20 ± 0.05

oxygen partial pressure P_{O_2} and can be described by

$$\log J_0 = \text{Constant} - \frac{\frac{2}{n}\Delta H_\alpha^0}{RT} \quad (9)$$

Enthalpy of formation of the considered defects in the NiO single crystal, which is proportional to the slope of the thermionic emission isobars for all the oxygen partial pressure P_{O_2}, is summarized in Table II. As can be seen from Table II, enthalpy of formation of the considered defects in the NiO single crystal increases slightly from 1.0 to 1.2 eV with decreasing oxygen partial pressure in the range of 5×10^1 to 5×10^{-2} Pa. Similar behaviour was observed in the electrical conductivity [6, 13] and trace diffusion studies [20] of NiO single crystal in the nearly same temperature and oxygen partial pressure range. All these behaviours can also be explained by the presence in NiO single crystals of the predominant singly ionized nickel vacancies and a small amount of doubly-ionized nickel vacancies with somewhat different energies of its formation.

5. Conclusion

Thermionic emission studies were performed on NiO single crystals within the temperature range of 500 to 900 K and the oxygen partial pressure range of 5×10^{-2} to 5×10^1 Pa. The $P_{O_2}^{1/n}$ dependence has been observed for the thermionic emission and the n parameter describing the degree of ionization of nickel vacancies increased from 4.25 to 4.80 with increasing annealing temperature in the range of 500 to 900 K. The activation enthalpy of the thermionic emission increased slightly from 1.0 to 1.2 eV with decreasing oxygen partial pressure in the range of 5×10^1 to 5×10^{-2} Pa. All these behaviours can be explained by the presence in NiO single crystal in the above technological conditions of the predominant singly-ionized nickel vacancies and a small amount of the double-ionized nickel vacancies with somewhat different energies of formation. Thus the thermionic emission appears to be a new very useful, except for the electrical conductivity, trace diffusion and thermogravimetric methods, for studying point defects in NiO single crystals; it is advantageous since the thermionic emission current depend only on the concentration of the electrons in the conduction band whereas electrical conductivity depends on the different types of carriers and their mobility.

Acknowledgements

The author wishes to thank Dr J. Nowotny from the Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Krakow, for the critical and stimulating discussions and Dr J. Obłakowski from the Institute of Material Science, Academy of Mining and Metallurgy, Krakow, for kindly supplying the NiO single crystals. Experimental assistance of M. Kliniewska and G. Sierpęk is also greatly appreciated. The work was supported by the Polish Academy of Sciences through Special Funds "Catalysis" Grant 03.10.2.

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Received 6 September
and accepted 22 September 1983