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Nonstoichiometry and hole doping in NiO

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Abstract. We have study by means of DFT+U and thermodynamic calculations the doping response of the p-type transparent oxide NiO. We have found from the calculated defect formation enthalpies that Ni vacancy, not the O interstitial, is the main source of nonstoichiometry in NiO. On the other hand, the calculated free-hole concentration at room temperature of pure NiO remains very low compared to the concentration of Ni vacancies; this is due to the too large ionization energy of the Ni vacancy. The free-hole concentration can be strongly increased by extrinsic dopants with a more shallow donor as it is illustrated for the case of Li.

Keywords: Nickel oxide, formation energies, intrinsic defects, defect levels, hole doping
PACS: 71.15.Nc, 71.20.Mq, 71.55.Cn, 72.20.Jv, 72.80.Sk

INTRODUCTION

NiO has been one of the most studied wide-gap oxides because of its hole dopability (p-type behavior), which is thought it is due to the nonstoichiometry nature of NiO (cation deficiency)[1, 2]. This p-type behavior together with its transparency ($E_g = 3.7$eV)[3] make NiO a promising material as a transparent conductor oxide (TCO) with applications in smart windows[4] and photovoltaics[5]. The microscopic origin of nonstoichiometry along with the conditions needed for a wide-gap oxide to be a hole conductor are now well understood[6]: (i) Hole-producing defects should have low formation energies. (ii) Such acceptors must have energetically shallow electrical levels. (iii) Hole killers such as anion vacancies, cation interstitials, which prevent hole doping should have high formation energies. Here we investigate theoretically these conditions for transparent conductivity due to the nonstoichiometry in oxides.

METHOD OF CALCULATION

All total energies, atomic forces and magnetic moments were calculated via first-principles using the projector augmented wave GGA+U method as implemented in the VASP code[7, 8]. We calculate the formation enthalpy[9] $\Delta H_{\mathrm{D,q}}(E_F,\mu)$ of defect D in charge state q (D = Ni or O vacancies, Ni or O interstitials, and Li impurity) as a function of the Fermi energy E_F and the chemical potential μ of Ni, Li and O using the supercell method. The calculated supercell total-energies are corrected for deficiencies associated with the supercell formalism and with the GGA+U approximation according to Ref. [9]. The thermodynamic simulations for the oxide stoichiometry and the carrier densities at realistic growth conditions are done such that the oxygen chemical potential, $\Delta\mu_{\mathrm{O}}$, for the O_2 gas phase is a function of the temperature T and pressure P[10, 11].

RESULTS AND DISCUSSION

We have found that GGA not only underestimate the calculated band gap of NiO, furthermore, it predicts NiO to be unstable compared to Ni_2O_3 for all the range of chemical potentials ($\Delta\mu_{\mathrm{Ni}}$, $\Delta\mu_{\mathrm{O}}$), in clear contradiction to the experimental data as it is illustrated in Fig. 1(a). In order to fix this shortcoming, we have used the GGA+U method, where we have chosen the Coulomb and exchange energy parameters with values of $U = 4.3$ eV and $J = 1$ eV for the Ni d shell. This recovers the stability of NiO compared to Ni_2O_3 (Fig. 1(b)). The estimated U and J values are in very good agreement to the ones estimated for the linear response approach[12]. Figure 1(b) illustrates the range of possible growth conditions between the Ni-rich/O-poor limit [$\Delta\mu_{\mathrm{Ni}} = 0$ eV, $\Delta\mu_{\mathrm{O}} = -2.36$ eV], and the extreme O-rich/Ni-poor limit, the Ni_2O_3 boundary [$\Delta\mu_{\mathrm{Ni}} = -2.26$ eV, $\Delta\mu_{\mathrm{O}} = -0.1$ eV].

Figure 2 shows the calculated formation enthalpies for the intrinsic defects in NiO. For Ni-poor/O-rich conditions the most important defect is the Ni vacancy (V_{Ni}), which has $\Delta H < 1$ eV. The other intrinsic defects: O vacancy (V_{O}), Ni interstitial (Ni_i) and O interstitial (O_i) have a high formation energy (above 2 eV). Then, V_{Ni} is the cause of nonstoichiometry in NiO. On the other hand, at these chemical potentials, condition (iii) for hole dopability is obtained as free-holes are no compensated by intrinsic donors. However, because of V_{Ni} transition levels are not shallow enough ($\varepsilon(0/-) = E_v + 0.48$ eV and $\varepsilon(-/2-) = E_v + 0.72$ eV), the free-hole concentra-

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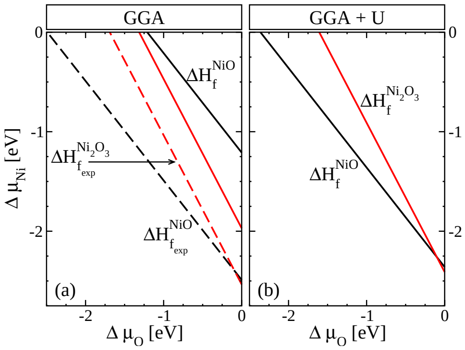

FIGURE 1. Ni chemical potential $\Delta\mu_{\mathrm{Ni}}$ as a function of the O chemical potential $\Delta\mu_{\mathrm{O}}$, as derived from the compounds stability conditions $x\Delta\mu_{\mathrm{Ni}} + y\Delta\mu_{\mathrm{O}} = \Delta H_f(\mathrm{Ni}_x\mathrm{O}_y)$ of different stoichiometries. (a) GGA calculated values are represented by solid lines and experimental values by dashed lines. (b) GGA+U calculated values.

tion at room temperature ($p_{298\mathrm{K}}$) stays below $10^{15}\mathrm{cm}^{-3}$ (see Fig. 3(a)). For Ni-rich/O-poor conditions the main defect is V_{O}, with a formation energy close to 1 eV, which implies higher concentrations of this defect. However, due to the its deep donor levels it does not produce free-electrons.

In order to increase the hole doping concentration, we have considered extrinsic doping in the case of $\mathrm{Li}_{\mathrm{Ni}}$. Figure 2 shows that $\Delta H < 1$ eV, resulting in a high solubility of this dopant (up to $2 \times 10^{21}\mathrm{cm}^{-3}$ at $T = 1000\mathrm{K}$ and P_{O_2}). Due to the more shallow energy of the transition level ($\varepsilon(0/-) = E_v + 0.25$ eV), the calculated free-hole concentration $p_{298\mathrm{K}}$ reach up to $10^{19}\mathrm{cm}^{-3}$.

In conclusion, NiO is a p-dopable material because hole killer defects have very high formation enthalpies for suitable conditions. However, due to the fact that V_{Ni} transition levels are not sufficiently shallow, the concentration of free-holes stays low. But, appropriate doping with extrinsic acceptors like Li leads to high concentration of free-holes.

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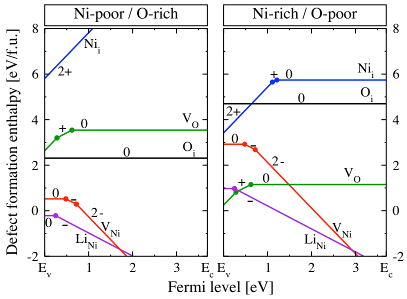

FIGURE 2. Defect formation enthalpies for NiO. The dots mark transition levels between different charge states. Ni-poor/O-rich conditions are limited by $\mathrm{Ni_2O_3}$ (Fig. 1(b)). Ni-rich/O-poor conditions are limited by Ni metal. The Li chemical potential is limited by the formation of $\mathrm{Li_2O}$.

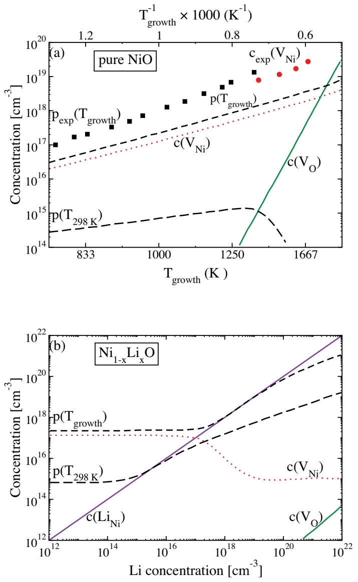

FIGURE 3. Calculated concentration of defects and holes (p) for NiO as a function of growth temperature T_{growth} and for O-rich conditions ($P(O_2) = 1$ atm). (a) Pure NiO and (b) Li-doped NiO. $p_{298\mathrm{K}}$ is calculated after thermal quenching. Experimental data (filled squares and circles) are taken from Refs. [13, 14].

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