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SUBMITTED TO: MRS Conference Proceedings
Nov. 28-Dec. 2, 1994, Boston, MA

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Abstract

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The structure and energy of surfaces in NiO have been studied by atomistic calculations employing short range Buckingham potentials fitted to properties of NiO. The polarizability of lattice anions is included by using the shell model. The results show that the surface energy depends strongly on surface orientation, and the {100} surface has the lowest energy. Surfaces with higher energy prefer to reconstruct into {100} facets to lower their energy and to stabilize their structure.

Introduction

Surfaces in oxide ceramics play an important role in determining material properties, such as mechanical strength, cleavage behavior and crystal growth, etc, [1]. The purpose of this work is to study the energy and structure of surfaces in NiO. The reason to choose NiO is that it has the NaCl type structure, which is the largest isostructural family among the transition metal oxides [2]. Oxides with this structure, such as MgO, have been found to facet into {100} surfaces [3]. Furthermore, solid solutions of MgO and NiO have been found to exhibit morphology changes under various compositions [4]. Knowledge of the energy and structure of surfaces with this lattice type is therefore important in understanding their properties. Although the calculations are based on interionic potentials which fit the properties of NiO, some of the results will have general relevance for other materials with the same structural type.

Computational Methodology

The interionic forces in NiO have been described in term of Coulomb long range potential and Buckingham short range potential, and the latter has been combined with the shell model to include polarisation of anions [5]. In this model, an O ion is treated as a positive core with a negative shell connected harmonically by a spring (with spring constant k). The short range interactions are between a Ni ion and an O shell and between O shells. The Buckingham potentials have been fitted to properties of NiO [6], which include the lattice parameter, the lattice energy, the elastic constants and the dielectric constants. From these fittings the spring constant k and the charge of the O shell, q , have also been obtained. The value of q is $-2.04e$, so that the O core has a charge of $0.04e$, where e is the electron charge.

Surface relaxation was carried out using the program MARVIN, and detailed explanations of this program have been described elsewhere [7]. The simulation method is similar to what has been used previously [8,9].

Results and Discussions

1. Energies of $\{hk0\}$ surfaces

A $(hk0)$ surface in NaCl lattice is a non-polar surface, i.e., there is no dipole moment in the direction perpendicular to the surface plane before relaxations. Such surfaces can be stabilized. The calculated results of surface energies, γ , of various $(hk0)$ ($h \leq k$) surfaces are illustrated in Fig.1, in which θ is the misorientation angle of a $(hk0)$ from the (010) surface around the $[001]$ axis. Each θ uniquely defines a $(hk0)$ surface, because all $(hk0)$ surfaces share the common zone axis $[001]$. The value of θ has been chosen from 0 to 45° , due to the four-fold symmetry of the $[001]$ direction and the mirror symmetry of the (011) plane.

Fig.1 shows that the dependence of γ on θ is monotonic, both before and after relaxation. Furthermore, the variation of γ with surface orientation is quite large, ranging from the minimum value of 1.17J/m^2 for the relaxed (010) surface to the maximum value of 2.98J/m^2 for the relaxed (110) surface. This is consistent with the experimental observation that in NiO and other metal oxides with the NaCl structure cleavage always takes place along the $\{100\}$ plane [1].

Fig.1. The calculated surface energy γ , as a function of misorientation angle, θ .

Fig.2. Schematic diagram of the structural decomposition of the $(hk0)$ surface.

The monotonic dependence of γ on θ can be well understood from atomic structures of these surfaces. In the NaCl type lattice, vicinal surfaces with Miller indices $(h10)$ can be well described as monatomic steps distributed uniformly on $\{100\}$ terraces [10]. Such a description can be generalized to any $(hk0)$ surface except that the distribution of the monatomic steps is usually not uniform except for $k=1$ [11]. This is illustrated schematically in Fig.2. For a given $(hk0)$ surface, the structure can be decomposed into h monatomic steps distributed on p (010) terraces having interionic distances $k_1, k_2, \dots, k_p$, in the $[100]$ direction. The total length of the

(010) terrace is $k_1+k_2+\dots+k_p=k$. The density of surface steps, α , in the direction $[\bar{k}h0]$ is $\alpha=2\sin\theta/a$, where a is the lattice parameter. The energy of a $(hk0)$ surface, $\gamma^{(hk0)}$, therefore consists of the terrace energy $\gamma^{(010)}$, the step energy γ^{step} , and the interaction energy between steps, γ^{int} , and can be written as:

$$\gamma^{(hk0)} = \gamma^{(010)}\cos\theta + \gamma^{\text{step}}\alpha + \gamma^{\text{int}}(\alpha)\alpha$$

Fitting of the calculated surface energies before relaxation leads to $\gamma^{(hk0)} - \gamma^{(010)}\cos\theta = 7.58 \times 10^{-10} \alpha$, which indicates that before relaxation there is almost no interactions between steps, and the unrelaxed step energy is 7.58×10^{-10} J/m. This is close to the previous result from a perfect geometry calculation [12], which gives a value of 8×10^{-10} J/m, and to the result from simulations [10], which gives a value of 8.16×10^{-10} J/m. The fitting of the relaxed surface energies leads to $\gamma^{(hk0)} - \gamma^{(010)}\cos\theta = 3.32 \times 10^{-10} \alpha + 27.2 \times 10^{-30} \alpha^3$. Thus the energy of the relaxed step is 3.32×10^{-10} J/m, which is much less than the unrelaxed value. The interaction between steps, $\gamma^{\text{int}}(\alpha)$, is strongly repulsive, and increases with the square of the step density α . This agrees with the result obtained from the elastic continuum theory [18], and suggests that the interaction between steps is elastic in nature [11].

2. Reconstruction of $(hk0)$ surfaces

The above results show that the (110) surface has the highest surface energy among all the $(hk0)$ surfaces. Its structure projected onto the (001) plane is shown in Fig.3(a). The black and white circles represent Ni ions and O ions, respectively. Behind each Ni ion along the [001] direction there is an O ion and vice versa. The primitive cell of this surface is $1/2[110] \times [001]$. The relaxed surface energy is 2.98 J/m^2 .

Fig.3. Structure of the (110) surface projected on the (001) plane; (a) flat surface, (b) reconstructed surface with unit cell 2×1 , (c) reconstructed surface with unit cell 4×1 .

If the unit cell is chosen to be 2×1 , i.e. with dimensions $[110] \times [001]$, and ions on alternate [001] columns are removed from the outermost layer, the resulting structure is shown in Fig.3(b). This corresponds to the (110) surface facetting into $\{100\}$ surfaces. The relaxed surface energy is

2.00J/m², which is much smaller than that without reconstruction, so the reconstruction is favored. Such missing-row reconstruction shown in Fig.3(b) has also been found at surfaces in f.c.c. metals, although the direction of the missing-rows is different [13]. Furthermore, if in general the unit cell is chosen to be $m \times 1$, where m is an integer, then following a similar procedure as for the 2×1 unit cell to remove some columns of ions to create $\{100\}$ surface facets, it is found that the larger the m , the smaller the relaxed surface energy, as is illustrated in Fig.4. In this figure, ρ is the density of $\{100\}$ facets in the $[1\bar{1}0]$ direction and equals $\sqrt{2}/m$, γ^{mx1} is the relaxed surface energy of the reconstructed (110) surface with unit cell $m \times 1$. The scattered symbols are from direct calculations, and the solid curve is from functional fitting, which leads to: $\gamma^m = 1.66 + 0.10\rho + 11.17\rho^2$ (J/m²). The first term, 1.66J/m², is the ideal energy value of the reconstructed surface if interactions between $\{100\}$ facets are ignored. The fitting indicates that the interaction between facets is repulsive, and increases with increasing density of facets. Such interaction vanishes gradually as the size of facets grows. The reconstructed surface structure with unit cell 4×1 is shown in Fig.3(c).

Fig.4 Energies of reconstructed (110) surfaces as a function of density of $\{100\}$ facets in the $[1\bar{1}0]$ direction.

	γ (J/m ²)	γ' (J/m ²)
(120)	2.002	1.680
(130)	1.700	1.542
(230)	2.352	1.833

Table 1. Energies for some other $(hk0)$ surfaces without and with reconstructions

Similar reconstructions of $(hk0)$ surfaces into $\{100\}$ facets have also been found for other surfaces, such as the (120) , (130) and (230) surfaces [14]. Their surface energies without and with reconstructions, denoted as γ and γ' , respectively, are summarize in Table 1.

3. Reconstruction of (111) surfaces

The $\{111\}$ surface is a polar surface in NiO structure, and is not stable in its perfect state [15]. The projected structure of this surface on the (111) plane is shown in Fig.5. In this and the following figures the shaded circles represent Ni ions and the white circles O ions. The solid square represents the unit cell on the surface. One way to stabilize a (111) surface is to create it in a way such that the structure terminates with only complete octopolar $(\text{NiO})_4$ molecules [16,17].

Each $(\text{NiO})_4$ molecule is the basis of the NiO lattice if its structure is treated as simple cubic, as shown in Fig.6. The (111) surface created in this way is shown in Fig.7(a) as projected on the (111) plane, and in Fig.7(b) as viewed from an oblique angle. Such reconstructed (111) surface has no dipole moment along the surface normal, because the dipole for a complete octopolar $(\text{NiO})_4$ molecule is zero. The (111) surface structure can thus be stabilized. Comparing Figs.7(a)(b) with Fig.5, it can be seen that the perfect flat {111} surface reconstructs into a ragged structure which can also be considered as micro-facets of the {100} surface. The surface energy is found to be 5.25J/m^2 and 2.62J/m^2 before and after relaxations, respectively. If the interactions between the {100} facets is ignored, the surface energy should be $\sqrt{3}\gamma^{(100)}$, which equals 2.03J/m^2 . So the results indicate that, similar as the (110) surface, the interaction between {100} facets on the (111) surface is repulsive, and should be expected to decrease as the {100} micro-facets grow. Such a result is consistent with the LEED observation that, in MgO, which has the same structure as NiO, (111) surface facets into {100} surfaces [3]. It also suggests an alternative explanation for the observation that NiO can be stabilized into {111} surface [4].

Fig.5. Structure of the perfect (111) surface projected on the (111) plane.

Fig.6. Structure of the octopolar $(\text{NiO})_4$ molecule.

Fig.7. The structures of the reconstructed (111) surface; (a) projected on the (111) plane, and (b) viewed obliquely.

Conclusions

Energy of (hk0) surface increases in the monotonic way with the increasing misorientation angle from the (010) surface. This was explained by treating the (hk0) surface structure as monatomic steps distributed on (010) terraces. The energy of the monatomic step is 7.58J/m and 3.32J/m before and after relaxation, respectively. The interaction between steps is repulsive and increases with step density as the power of two. (hk0) surfaces with higher energies prefer to reconstruct into (100) surface facets, and the interaction between (100) facets is repulsive and converge to zero as size of facets grows. The (111) surface can be stabilized by reconstruction into {100} micro-facets. The relaxed surface energy is 2.62J/m².

Acknowledgements

We would like to acknowledge Drs. R. Grimes and S. Vyas for providing their potentials, and to acknowledge Dr. D. Gay for helpful discussions regarding MARVIN program. This research was supported by Department of Energy, Office of Basic Energy Science.

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