TITLE: RECONSTRUCTION OF SURFACES IN NiO

AUTHOR(S): M. Yan
S. P. Chen

SUBMITTED TO: Proceedings, American Ceramics Society Annual Conference
May 1, 1995, Cincinnati, OH

By acceptance of this article, the publisher recognized that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution or to allow others to do so for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
RECONSTRUCTION OF SURFACES IN NiO

M. Yan and S. P. Chen
Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545

ABSTRACT

We studied the reconstructions of surfaces in NiO by atomistic simulations which utilize Buckingham short range potentials and the shell model. It was found that \{hk0\} surfaces prefer to reconstruct into \{100\} surface facets which has the lowest energy. The interaction between these \{100\} facets is repulsive and converges to zero as size of facets grows. The \{111\} surface can be stabilized by reconstruction into \{100\} micro-facets.

INTRODUCTION

Reconstruction of surface has been found to be a common feature in metallic systems, from both experiments and theoretical calculations in the recent years [1-3]. The study of reconstruction in oxide ceramics, however, is still very limited. In this work we studied the reconstruction of \{hk0\} and \{111\} surfaces in NiO, which has the NaCl structure. From experiments it has been observed that the \{110\} and \{111\} surfaces in MgO, which also has the NaCl structure, facet into \{100\} surfaces [4].

The interionic forces in NiO have been described by Coulomb long range and Buckingham short range potentials, and the latter has been combined with the shell model to include polarization of anions [5], i.e. an O ion is treated as a positive core and a negative shell connected harmonically by a spring. The Buckingham potentials have been fitted to properties of NiO by Grimes, et al, which include the lattice parameter, the lattice energy, the elastic constants and the dielectric constants [6, 7].

Surface relaxation was carried out using the program MARVIN [8]. The simulation method is similar to what has been used previously [9, 10].

RESULTS AND DISCUSSIONS

1. Reconstruction of \{hk0\} surfaces

A \{hk0\} surface in NaCl lattice is a non-polar surface, and the calculated surface energies, $\gamma$, are illustrated in Fig.1 as the function of the rotation angle, $\theta$, from the \{010\} surface. It can be seen that the dependence of $\gamma$ on $\theta$ is monotonic, both before and after relaxation. The variation of $\gamma$ with $\theta$ 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/m² 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]. The reason for the monotonic dependence between the surface energy and the surface orientation has been explained before [7, 12, 13].

![Graph showing the calculated surface energy, γ, as a function of the rotation angle, θ.](image)

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

Fig.2(a) shows the structure of the (110) surface projected onto the (001) plane. 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.

If the unit cell is chosen to be 2x1, i.e. with dimensions [110]x[001], and ions on alternate [001] columns are removed from the outermost layer, the resulting structure is shown in Fig.2(b). This corresponds to the (110) surface facetting into two {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.2(b) has also been found at surfaces in f.c.c. metals, although the direction of the missing-rows is different [14]. Furthermore, if in general the unit cell is chosen to be mx1, where m is an integer, then following a similar procedure as for the 2x1 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.3. In this figure, ρ is the density of {100} facets in the [110] direction and equals \( \frac{\sqrt{2}}{m} \), \( \gamma^{mx1} \) is the relaxed surface energy of the reconstructed (110) surface with unit cell mx1. The scattered symbols are from direct calculations, and the solid curve is from functional fitting, which leads to:

\[
\gamma^{mx1} = 1.66 + 0.10\rho + 11.17\rho^2 \text{(J/m}^2\text{)}
\]

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 the faceted surface grows, i.e. as $\rho \rightarrow 0$. The reconstructed surface structure with unit cell 5x1 is shown in Fig.2(c).

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

![Fig.2. Structures of the (110) surface projected on the (001) plane; (a) flat surface; (b) reconstructed one with unit cell 2x1; (c) reconstructed one with unit cell 5x1.](image)

2. Reconstruction of the (111) surface

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.4. The shaded circles represent Ni ions and the white circles O ions. One way to stabilize a (111) surface is to create it in a way such that the structure terminates with only complete octopolar (NiO)$_4$ molecules [16, 17]. Each (NiO)$_4$ molecule is the basis of the NiO lattice if its structure is treated as simple cubic, as shown in Fig.5. The (111) surface created in this way is shown in Fig.6(a) as...
Table 1. Energies for some other \{hk0\} surfaces without and with reconstructions

<table>
<thead>
<tr>
<th>(\rho) (x10^{10} \text{ m}^{-1})</th>
<th>(\gamma) (J/m²)</th>
<th>(\gamma') (J/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(120)</td>
<td>2.002</td>
<td>1.680</td>
</tr>
<tr>
<td>(130)</td>
<td>1.700</td>
<td>1.542</td>
</tr>
<tr>
<td>(230)</td>
<td>2.352</td>
<td>1.833</td>
</tr>
</tbody>
</table>

Fig. 3 Energies of reconstructed (110) surfaces as a function of density of \{100\} facets in the [110] direction.

Projected on the (111) plane, and in Fig. 6(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 (NiO)_{4} molecule is zero. The (111) surface structure can thus be stabilized. Comparing Figs. 6(a)(b) with Fig. 4, 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/m² and 2.62J/m² 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/m². So the results indicate that, similar to 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 [4]. It also suggests an alternative explanation other than impurity segregations for the observation that NiO can be stabilized into \{111\} surface [18].

CONCLUSIONS

Energy of a \{hk0\} surface increases in the monotonic way with the increasing rotation angle from the (010) surface. The \{hk0\} surfaces with higher energies prefer to reconstruct into \{100\} surface facets. The interaction between these \{100\} facets is repulsive and converges to zero as the size of facets grows. The (111) surface can be stabilized by reconstruction into many \{100\} micro-facets, and the relaxed surface energy is 2.62 J/m².
Fig. 4. The structure of the perfect (111) surface projected on the (111) plane.

Fig. 5. The structure of the octopolar (NiO)$_4$ molecule.

Fig. 6. Structures of the reconstructed (111) surface; (a) projected on the (111) plane; and (b) viewed obliquely.

ACKNOWLEDGMENTS

We acknowledge Drs. R. W. Grimes and S. Vyas for providing their potentials, and acknowledge Dr. D. H. Gay for helps regarding MARVIN program. We also thank Dr. A. F. Voter for helpful discussions. This research
was supported by Division of Materials Science, Office of Basic Energy Science of Department of Energy.

REFERENCES