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## The structure of higher defective ZnO(10 $\bar{1}$ 0)

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### Abstract

The surface structure of clean and defective ZnO(10 $\bar{1}$ 0) have been studied using ab initio plane wave density functional theory. Two models of surface defects have been examined; an oxygen vacancy within the surface Zn–O dimer and an oxygen vacancy in the second layer of the material. Previous models of CO oxidation on this surface have invoked the formation of isolated second layer defects. In the current study we show that the formation of such a defect costs 1.01 eV more energy than the formation of a vacancy within the dimer bond and hence models of catalytic activity that invoke the formation of isolated second layer defects need to be re-examined.

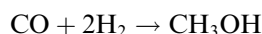
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Zincite (ZnO) is an ionic semiconductor which has a wide range of technological uses. These include its use as a white pigment and opacifier, its use in the rubber industry where it shortens the time of vulcanization, and also applications in catalysis and gas sensing systems [1]. In combination with copper, ZnO forms an important industrial catalyst for both the water–gas shift reaction [2]



and for methanol synthesis [3]



A detailed understanding of the surface chemistry of ZnO responsible for its role in sensing and catalyst applications is lacking. This is due to the very complex nature of the material's surfaces. The material can expose a wide range of both polar and non-polar surfaces, can expose acidic Zn and basic O sites, and has a complex defect chemistry. The most important class of defects for the majority of oxide surfaces are point defects, typically either anion or cation vacancies. For ZnO it is known that the most commonly occurring defects are oxygen vacancies [4–6].

The important role of defects in determining the chemical reactivity of ZnO surfaces has been demonstrated in a number of experimental studies [7]. In particular, the interactions of CO with ZnO (important for its role in methanol synthesis) have been found to be strongly dependent on defect

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concentration. Indeed, adsorption of CO is thought to result in the formation of CO<sub>2</sub> and an oxygen defect on the (10 $\bar{1}$ 0) surface. As the surface is exposed to CO, the surface conductivity is found to rise due to the presence of oxygen point defects [4]. Possible models of this process have been put forward which involve the formation of isolated oxygen defects in the second layer of the material [4]. Simulation of the material by ab initio calculations is ideally suited to addressing the nature of the defective surfaces.

Zinc oxide crystallises in the Wurtzite structure in which the cations are tetrahedrally co-ordinated with oxygen ions in the bulk. The atomic planes perpendicular to the (10 $\bar{1}$ 0) direction consist of equal numbers of zinc and oxygen ions and can be thought of as consisting of rows of zinc–oxygen dimers. These dimers are then bonded to dimers in the next layer as shown in Fig. 1. Consequently, the proposed models of defect formation in the second layer involve the removal of a fully co-ordinated oxygen ion from the lattice. One alternative mechanism involves the removal of a first layer oxygen ion from a surface dimer bond. In the current study the energetics of these two types of defects on the ZnO(10 $\bar{1}$ 0) are investigated.

The calculations were performed employing plane wave density functional theory as implemented in the CASTEP code [8,9]. Core electron states were represented by the use of ultrasoft

pseudo-potentials [10,11], and the calculations were found to be converged to better than 0.01 eV for a plane wave cut off energy of 400 eV. The electronic ground state was found through conjugate-gradient minimisation of the total energy with respect to the plane wave coefficients. Mechanical equilibrium was achieved by relaxation of the ionic positions using a modified Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimisation algorithm. Electron exchange and correlation were described within the generalised gradient approximation [12]. Brillouin zone sampling was performed on a Monkhorst–Pack grid with the density of points determined from a spacing of 0.05 Å<sup>-1</sup>.

Initially, a full optimisation of the clean, unreconstructed ZnO(10 $\bar{1}$ 0) surface was performed. This surface has been the subject of a number of previous theoretical studies [13–20]. The current studies produce results in line with the existing literature, although the tilt angle of the surface dimer is slightly larger than has been previously observed, as is the contraction of the surface dimer bond. The results for the clean surface, along with previously optimised surface structures are summarised in Table 1.

A full geometric optimisation of two possible oxygen defect structures was then performed. The first model consist of an oxygen defect in the first layer of the material. The removal of an

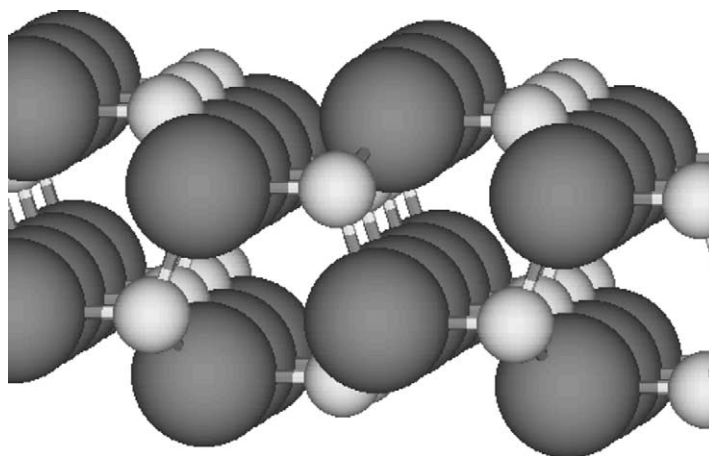


Fig. 1. The ZnO(10 $\bar{1}$ 0) surface.

Table 1  
The geometric structure of the clean ZnO(10 $\bar{1}$ 0) surface

|                     | $x_1$ | $x_2$ | $z_1$ | $z_2$ | $d$   | $\Delta d$ | $\theta$     |
|---------------------|-------|-------|-------|-------|-------|------------|--------------|
| Bulk Expt           | 0.613 | 2.605 | 0.938 | 0.938 | 1.992 | 0.0        | 0.0          |
| Bulk HF [13]        | 0.600 | 2.621 | 0.950 | 0.950 | 2.021 | 0.0        | 0.0          |
| Bulk HF + corr [13] | 0.584 | 2.551 | 0.924 | 0.924 | 1.967 | 0.0        | 0.0          |
| Bulk B3LYP [20]     | 0.640 | 2.605 | 0.938 | 0.938 | 1.998 | 0.0        | 0.0          |
| Bulk (this study)   | 0.617 | 2.626 | 0.944 | 0.944 | 2.009 | 0.0        | 0.0          |
| Surf Expt [14]      | 0.62  | 2.59  | 0.54  | 0.94  | 2.01  | +0.9       | 11.5 $\pm$ 5 |
| TB [15–17]          | 0.98  | 2.82  | 0.53  | 1.10  | 1.926 | –3.3       | 17.2         |
| HF [13]             | 0.707 | 2.581 | 0.691 | 0.766 | 1.876 | –7.2       | 2.31         |
| HF + corr [13]      | 0.683 | 2.521 | 0.678 | 0.758 | 1.839 | –6.5       | 2.48         |
| HF + corr [13]      | 0.683 | 2.521 | 0.678 | 0.758 | 1.839 | –6.5       | 2.48         |
| LDA [18,19]         | 0.534 | 2.365 | 0.623 | 0.738 | 1.835 | –7.9       | 3.59         |
| B3LYP [20]          | 0.705 | 2.602 | 0.626 | 0.777 | 1.905 | –4.9       | 5.20         |
| This study          | 0.804 | 2.646 | 0.659 | 0.903 | 1.858 | –7.8       | 7.48         |

oxygen from the surface dimer bond reduces the co-ordination of the first layer Zn atom within the dimer from 3 to 2. Similarly, two second layer zinc ions have their co-ordination reduced from 4 to 3. In the second model, we remove an oxygen ion from the second layer of the material. This reduces the co-ordination of two zinc ions in the first layer from 3 to 2, the co-ordination of a second layer atom from 4 to 3, and the co-ordination of a third layer ion also from 4 to 3. The defective surfaces are modelled as a (2  $\times$  2) super-cell, which is the smallest super-cell that maintains a bulk dimer between the defects on the surface.

The structure and surface energy of the model of a defect in the first layer is found to be converged for slabs containing eight layers of material. The model of a second layer defect is found to be converged for a 10-layer slab. The energy difference between these two structures is found to be 3.18 eV for a six-layer slab, 1.05 eV for an eight-layer slab and 1.01 eV for the ten layer slabs, with the first layer defect being more stable than defects in the second layer for all slab thicknesses. In both cases the majority of the bond lengths within the crystal remain essentially bulk like. For the first layer defect the largest displacement involves the rotation of the under co-ordinated Zn ion into the hole left by the removal of the oxygen ion. The neighbouring surface dimer bonds have essentially the same structure as the surface bonds on the

perfect (10 $\bar{1}$ 0) surface. For the second layer defect structure, the under co-ordinated zinc ions within the first layer dimer sink into the hole left by the removal of the oxygen ion. This leads to a 3° increase in the tilt angle of the surface dimer bonds. However, again, all bonds lengths remain very similar to those observed for the clean, unreconstructed ZnO(10 $\bar{1}$ 0) surface.

The high concentration of defects within our current models gives rise to a metallic defect band on the surface in line with experimental observations of rising conductivity as a function of CO oxidation, and hence of surface oxygen vacancy formation.

First layer defects may be expected to be more stable than second layer defects as they produce less perturbation of the co-ordination numbers of the ions within the material. However, models of CO oxidation on the ZnO(10 $\bar{1}$ 0) surface have often invoked the creation of isolated defects in the second layer [4]. Given the large energy difference between the formation of the isolated first and second layer vacancies found here, such models are unlikely. However, we cannot, on the basis of the current study, eliminate the possibility of the formation of clusters of defects within the second layer during the oxidation reaction. The current study shows that if CO oxidation occurs via the creation of isolated defects, then the reaction is likely to proceed via the formation of vacancies within the surface dimer bond.

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