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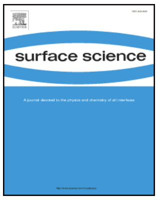

Cu cluster deposition on ZnO$\left(10\bar{1}0\right)$: Morphology and growth mode predicted from molecular dynamics simulations☆

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ABSTRACT

Clusters of Cu on ZnO surfaces are established catalyst systems produced by vapor deposition of Cu that consolidates into discrete clusters. Factors such as the geometry of the ZnO surface, the nature of the interface between Cu and ZnO, and the size and distribution of metal clusters strongly control the reactivity and stability of the catalyst. Here, we report on the development and use of charge-optimized many-body (COMB) potentials to model the deposition and subsequent evolution of Cu clusters on ZnO$\left(10\bar{1}0\right)$ using classical molecular dynamics (MD) simulations. The simulations predict that the deposited Cu spreads to form two-dimensional (2D) clusters until the coverage is above 0.4 monolayers (ML). Thereafter, the 2D clusters grow thicker with increasing Cu coverage and finally form three-dimensional (3D) clusters. The predictions are compared to published experimental data and help to elucidate aspects of the growth that are currently the subject of controversy in the literature. In addition, the influence of such factors as incident cluster deposition energy, ZnO surface temperature, and different supports on the surface morphology of the Cu clusters are examined. The results are expected to provide useful guidance for the improved production of dispersed Cu clusters on ZnO surfaces.

1. Introduction

Over the past decade, the Cu/ZnO system has been widely used as a catalyst for the synthesis of methanol via hydrogenation of CO and CO_2 [1], water–gas shift reaction for removal of CO [2,3], and the production of hydrogen by steam reforming of methanol [4]. As a result, this system has been widely studied in an attempt to better understand the mechanisms by which it functions with the hope that the same principles may be used to create catalysts with greater activity and selectivity. Because factors such as the surface geometry, the interface between the metal and oxide, and the size and distribution of metal clusters are thought to strongly control the reactivity and stability of the catalyst [5,6], these issues have motivated many investigations of Cu growth on several ZnO surfaces.

To date, there have been several surface studies to characterize Cu growth on polar [7–11] and nonpolar ZnO surfaces [12–15] by techniques such as scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). Nevertheless, there are discrepancies in the nucleation sites and growth mechanisms suggested by the experimental data, presumably originating from differences in sample preparation and/or surface analysis techniques [13]. Therefore, atomistic modeling of Cu growth on ZnO is used to elucidate aspects of the growth that are subject to controversy in the literature [13,16,17] by excluding the effect of containment atoms and residual gas. In addition, it is expected to provide insights that are complementary to the experimental data, and ultimately to improve future catalyst design.

Here, a third-generation charge-optimized many-body (COMB) potential for ZnO is developed and used to model the ZnO$\left(10\bar{1}0\right)$ surface interacting with either a single Cu adatom or a beam of deposited and equilibrated Cu clusters in classical molecular dynamics (MD) simulations. The use of a reactive potential with dynamic charge [18,19], such as COMB, in the simulations under temperature and pressure conditions that are similar to those in the experiments is necessary to fully describe the potential nanometer-scale changes at the interface, including sintering of the Cu clusters, alloying with the oxide surface, and oxidation of the Cu during the growth process. The COMB predictions for ZnO properties and of adsorption and migration energies of Cu atoms on the ZnO$\left(10\bar{1}0\right)$ surface are compared to published experimental data and to the results of density functional theory (DFT) calculations. In addition, the MD simulation results are compared with STM results to explain some puzzling experimental observations. The simulations further explore the way in which the growth mode and final morphology of the Cu clusters are influenced by changes in the Cu incident deposition energy and surface temperature. Cu growth on ZnO is also

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compared to Cu growth on Cu to determine how the nature of the surface influences the predictions.

The rest of the paper is organized as follows: In Section 2, a description of the COMB3 potential is provided along with results that compare the predicted properties of wurtzite ZnO and Cu–Zn alloys with available experimental results and DFT calculations. In Section 3, the static predictions for the adsorption energy and migration barriers for Cu on ZnO$\left(10\bar{1}0\right)$ are given. This section also provides the results of the MD simulations, which include the effects of incident energy, ZnO surface temperature, and different supports on the growth and evolution of deposited Cu clusters. Finally, the conclusions are given in Section 4.

2. Simulation methodology

2.1. Charge-optimized many body (COMB) potential

In classical MD simulations, Newton's equations of motion are integrated and the forces on the atoms are determined with empirical potential functions. The use of accurate, transferrable potentials is therefore crucial to accurately model the material systems of interest. The atomic-scale calculations and simulations reported here are carried out using the third-generation COMB potential (COMB3). The development of COMB3 uses terms from the second-generation COMB potential (COMB2) [20] for electrostatic effects, the second-generation reactive empirical bond order (REBO2) [21] potential for short-range interactions, and the coordination function that was developed for the REBO potential for MoS_2 [22] systems. In particular, because of the replacement of the original Tersoff expression, which lacks the four-body dihedral term to capture the delocalized bonding in hydrocarbon systems, with short-range interaction terms used in REBO2, the COMB3 potential can be extended to C/H/O/N [23] systems. The complete details of the third-generation COMB formalism can be found in Refs. [23] and [24].

The procedure used for parameter fitting follows that outlined by Liang et al. [25]. In particular, element-specific parameters are fit for pure elements (O, Cu, and Zn) and bond-specific parameters are fit for Cu_2O and ZnO systems. The main strength of the COMB potential is its transferability. For example, the element-specific parameters for O and Cu, and their associated bond-specific parameters, are utilized from existing COMB potentials for the Cu/Cu_2O system [26]. As for the parameterization of the Zn/ZnO system, we used the same fitting strategy that was used previously for the COMB2 Zn/ZnO potential [23]. The potential details for the Cu/ZnO system in LAMMPS may be found in the Supplementary materials.

Table 1 lists the properties of the ZnO wurtzite phase predicted by the COMB3 potential reported here, in comparison with published experimental data, DFT calculations and previous second-generation COMB (COMB2) results [27]. The DFT calculations used to parameterize and validate the potential were carried out with the Vienna ab initio Simulation Program (VASP) [28–31] within the generalized-gradient approximation (GGA), using the Perdew–Burke–Ernzerhof (PBE) [32,33] exchange–correlation functional. The valence electron orbitals for zinc included the 3d and 4s orbitals, while the 2s and 2p electrons were considered for oxygen. A plane-wave basis with a 500 eV energy cutoff and a 6 × 6 × 6 Monkhorst–Pack k-point mesh were used. For the Cu–Zn alloys, the valence electron orbitals of 3d and 4s are considered for copper. A plane-wave basis with a 345 eV energy cutoff and a 6 × 6 × 6 Monkhorst–Pack k-point mesh were used. The convergence criteria were set at 1×10^{-5} eV and 1×10^{-2} $eV{\cdot}Å^{-1}$ for energies and forces, respectively, for ZnO and CuZn systems.

Table 1
Comparison of the properties of ZnO wurtzite phase predicted by the COMB2 and COMB3 potentials with values obtained from experiments and DFT calculations.

Properties	Exp.	DFT	COMB2	COMB3
a_0 (Å)	3.242	3.292	3.249	3.267
c_0 (Å)	5.187	5.293	5.213	5.189
c/a	1.600	1.608	1.604	1.582
E_c (eV/ZnO)	−7.520	−7.692	−7.440	−7.524
B (GPa)	136	134	147	138
C_{11} (GPa)	207	230	252	206
C_{12} (GPa)	121	82	129	114
C_{13} (GPa)	106	64	98	97
C_{33} (GPa)	210	247	267	217
C_{44} (GPa)	43	75	37	44
C_{66} (GPa)	–	74	57	47
$\gamma_{Cleave}\left(10\bar{1}0\right)$ (J/m²)		2.30	2.12	2.21
$\gamma_{Cleave}\left(11\bar{2}0\right)$ (J/m²)		2.50	2.31	2.33
$\gamma_{Cleave}(0001)/\left(000\bar{1}\right)$ (J/m²)		4.30	2.02	2.61
ΔE(ZnS-Wurtzite)(eV/ZnO)		0.013	0.008	0.021
ΔE(NaCl-Wurtzite)(eV/ZnO)		0.237	0.217	0.903
ΔE(CsCl-Wurtzite)(eV/ZnO)		1.358	0.958	1.225

From Table 1, it is clearly shown that the newly developed COMB3 potential exhibits good predictions as COMB2 potential on the cohesive energy and the elastic constants of the wurtzite phase. Most importantly, the incorrect surface energy predictions of the COMB2 potential have been improved in the new COMB3 potential, where the polar surfaces of wurtzite ZnO have higher cleavage energies than nonpolar surfaces. Nevertheless, because the stabilization effect for the ideal termination of the polar surfaces of ZnO involves charge compensation of the surface layers, the cleavage energy for the polar surfaces is not quantitatively captured in the current COMB potential. Therefore, in future work incorporating data related to the polar surfaces, such as cleavage energies or reconstructed surfaces, may improve the COMB potential description of the polar surfaces.

2.2. Fitting parameters for Zn–Cu interactions

The Cu–Zn interactions in COMB3 are explicitly parameterized for three specific Cu–Zn alloys [34], which are the α-brass Cu_3Zn (fcc), β-brass CuZn (bcc), and γ-brass Cu_5Zn_8($cI52$) phases, respectively. Table 2 lists the COMB3 predictions and makes a comparison to DFT and published experimental data. The heat of formation for the γ phase is properly calculated to be the lowest and the phase order prediction is correct. Although the bulk modulus of the γ phase is predicted to be larger than that measured experimentally, the correct phase order is of more important because of the focus on potential alloying during cluster deposition and metal thin film growth rather than mechanical properties of this alloy.

2.3. Details of the molecular dynamics simulation of cluster deposition and relaxation

Classical MD simulations are used to model Cu_6 deposition on the ZnO$\left(10\bar{1}0\right)$surface, where the forces on the atoms are determined via the COMB3 potential. Fig. 1 shows the deposition system which is composed of deposited Cu clusters and a ZnO surface slab. The dimensions of the ZnO surface slab are 72 Å × 74 Å × 70 Å and it consists of 36,960 atoms; the $\left[10\bar{1}0\right]$ direction is perpendicular to the plane of the surface.

Table 2
Properties of Cu–Zn alloys predicted by COMB3 compared to those from experiments and DFT calculations. The reference states for the enthalpies of formation are metallic fcc Cu and hcp Zn, which are −3.725 and −1.272 eV/atom, respectively.

Phases	Properties	Exp.	DFT+	COMB3
γ–Cu_5Zn_8	a_0 (Å)	8.86 [34]	8.88	8.88
	ΔH_f(kJ/mol)		−126	−138
	B (GPa)	123 [34]		156
β–CuZn	a_0 (Å)		3.34	3.36
	ΔH_f(kJ/mol)		−21	−48
α–Cu_3Zn	a_0 (Å)		2.97	3.01
	ΔH_f(kJ/mol)		−16	−36

+ Our DFT calculations.

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