（様式第 20）成果報告書

共同利用（産業利用トライアルユース：先端研究施設共用促進事業『みんなのスパコン』TSUBAME によるペタスケールへの飛翔） 成果報告書 平成 20 年度 課題種別「新規材料開発のための、オーダーN法による金属酸化物表面の第一原理シミュレーション」

利用課題名 新規材料開発のための、オーダーN法による金属酸化物表面の第一原理シミュレーション
英文：The order-N first-principles simulation of metal oxide surfaces for novel material development.

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邦文抄録（300 字程度）

遷移金属酸化物は触媒や塗料、電子デバイス等の開発において、非常に重要な役割を果たしている。遷移金属酸化物における研究課題の一つとして、触媒反応の活性と選択性における表面欠陥の影響が重要視されている。遷移金属酸化物の表面酸素欠陥はホストの系に対して構造および電子状態の変化を引き起こす。今回の利用においてはこれらの系に対するコンピューターシミュレーション技法を検討するために、非常に良く知られている酸化アルミニウムの系において点欠陥を持つモデルを構築、オーダー*N*法のDFT計算手法であるONETEPでシミュレーションを実行、結果の検証を行った。また、酸化ガリウム、酸化インジウムの系においても予備的な計算を行った。

英文抄録（100 words 程度）

Transition metal (TM) oxides are of great importance for heterogeneous catalysis, corrosion-protective coating of metals and microelectronic devices. An important issue in TM oxide-based material is the role of surface defects to the activity and selectivity of the catalyst. Oxygen vacancies at (TM) oxide surfaces (or in the bulk) alter the geometric and electronic structure of the host system. In the present study the oxygen vacancy scenarios was described for aluminum oxide, Gallium oxide and Indium oxide using ONETEP (Order-*N* Electronic Total Energy Package) a parallel density-functional theory code for large-scale first-principles quantum-mechanical calculations.

Keywords: ONETEP, oxide, vacancy, selectivity, catalysis, Order-N

背景と目的

Transition metal (TM) oxides constitute an important class of inorganic solids exhibiting a very wide variety of structures and electronic and magnetic properties that are due to the nature of the outer d states. They are of great importance for a number of a technological applications such as heterogeneous catalysis, corrosion-protective coating of metals and microelectronic devices. Furthermore, bulk defects play a significant role in determining surface properties where, for example, annealing to high temperatures is necessary. In turn, the host system will largely determine the properties of the vacancies. The expectation that a fundamental understanding (i.e., microscopic) of these defects will help to elucidate the effect that they have on the system's functionality has been the driving force for pursuing experimental and theoretical research on reduced materials. Point defects in TM oxides such as vacancies and interstitials account for the transport properties of ionic solids.The study of aluminum oxides is motivated by fundamental scientific interest as well as by their technological relevance, e.g., as support in heterogeneous catalysis. An important role in enhancing catalytic reactions is believed to be played by structural defects, in particular, oxygen vacancies, which act as adsorption centers for molecules or metallic clusters [1, 2]. Atomic-scale studies of such vacancies are exceedingly difficult, since insulating bulk oxides cannot be probed by many experimental techniques, such as scanning tunneling microscopy (STM). A way to circumvent this problem is to study ultrathin oxide films grown on conducting substrates. Because of the structural complexity of these films, the microscopic interpretation of experimental data remains a challenge.

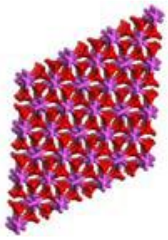
ONETEP is an *ab initio* electronic structure package for total energy calculations within density-functional theory. It combines 'linear scaling'; in that the total computational effort scales only linearly with system size, with 'plane-wave' accuracy, in that the convergence of the total energy is systematically improvable in the manner typical of conventional plane-wave pseudopotential methods. ONETEP was developed from the beginning as a parallel code [3, 4].We present recent progress on improving the performance, and thus in effect the feasible scope and scale, of calculations with ONETEP on parallel computers comprising large clusters of commodity servers. Our recent improvements make calculations of tens of thousands of atoms feasible, even on fewer than 100 cores. Efficient scaling with number of atoms and number of cores is demonstrated up to 32,768 atoms on 64 cores.

概要

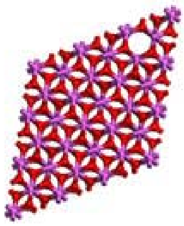
Oxygen vacancies have been detected and investigated using a variety of spectroscopic techniques; however, much has been learned recently about the structure of defective surfaces using scanning probe techniques. In spite of that, there are still difficulties in the experimental determination of the vacancy-induced lattice relaxations, and information about the vacancy formation energy (hence defect stability) is not always experimentally obtainable. Therefore, a great number of theoretical studies on oxygen removal from TM and RE oxides have appeared in the literature. In particular, isolated oxygen vacancies at differently oriented surfaces and in the bulk have received much attention. Strong interactions can occur between defects, causing them to cluster or order. Yet, isolated defects (or a low concentration of them) have been the natural starting point for the theoretical studies. Once a more accurate description of the surface electronic structure has been reached, the next logical step would be to re-inspect results of surface chemistry studies on TM and RE oxides, e.g., on the binding of selected adsorbates on reduced surfaces and the nature of reaction intermediates on easily reducible oxides. In this study we aim to look into the stability of the structure with vacancy concentration for TM and RE oxide, so far we are able to look into Al_2O_3, Ga_2O_3 and InO_2

結果および考察

In the present case we have tried to optimize different vacancy concentration in alpha alumina to propose a correlation to the vacancy concentration and activity through the formation energy.

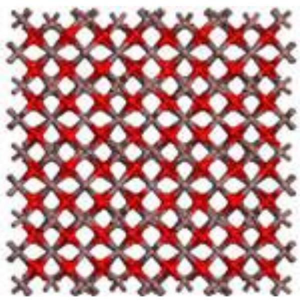


Composition: O324Al216



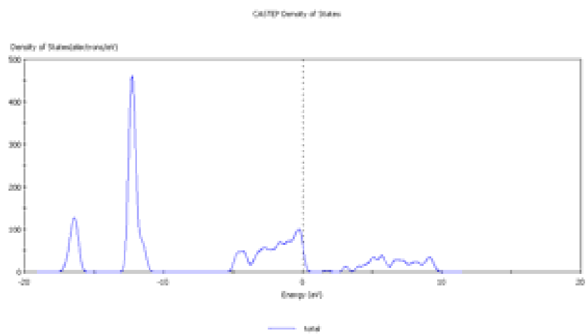
Composition: O318Al216

We have also calculated indium oxide without defect.

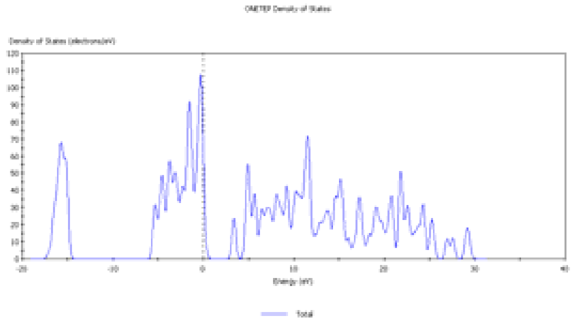


InO_2 without defect

CASTEP density of state

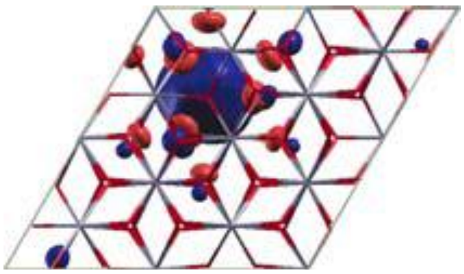


ONETEP density of state



We calculated density of states of aluminum oxide with ONETEP and the well validated DFT tool, CASTEP[5]. Keeping the band gap same ONETEP will allow one to see the distribution of bands in more detail. An appalling fact is the band distribution in the Indium oxide and it is certain that there will be more influence of vacancy in the band architecture.

The point is to see the activity at the defect or vacancy site after optimization. All calculations were performed with ONETEP with SINC basis function with 800 eV cut off and a force convergence of 0.0001 eV/angstrom and a stress convergence of 0.001 GP1.



Now look closely in the defect and wanted to compare the defect concentration with the formation energy and a swell the localized distortion of the lattice.

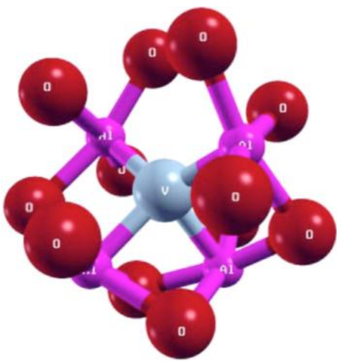


Table 1: Internal relaxation both with position and percentage with change in the layer location

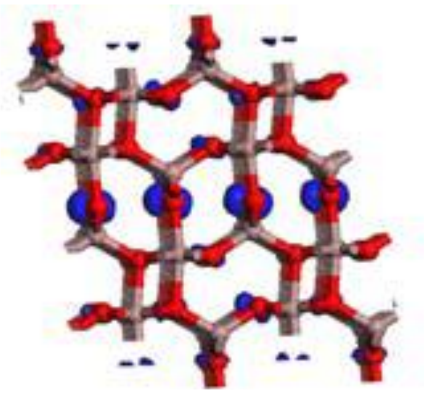
Optimized atom	O-2 vacancy d_i (Å)	d_f (Å)	%	Optimized atom	O-5 vacancy d_i (Å)	d_f (Å)	%
Al	1.703	1.503	−13.3	Al	1.878	1.926	2.5
Al	1.817	1.832	0.8	Al	1.975	2.016	2.0
Al	1.904	2.029	6.2	Al	1.949	2.064	5.6
O	2.613	2.576	−1.4	Al	2.012	2.095	4.0
O	2.634	2.569	−2.5	O	2.592	2.550	−1.6
O	2.634	2.581	−2.1	O	2.592	2.557	−1.4
O	2.709	2.692	−0.6	O	2.613	2.600	−0.5
O	2.757	2.750	−0.3	O	2.659	2.634	−1.0
O	2.757	2.707	−1.9	O	2.709	2.659	−1.9
O	2.768	2.768	0.0	O	2.754	2.704	−1.8
O	2.944	2.895	−1.7	O	2.768	2.802	1.2
O	2.944	2.864	−2.8	O	2.773	2.717	−2.1
				O	2.864	2.856	−0.3
				O	2.864	2.865	0.0
				O	2.878	2.879	0.0
				O	2.787	2.870	−0.3

Table 2: Calculated energy formation of surface oxygen vacancies in Alpha-Al_2O_3 (0001). The oxygen vacancy in the second or fifth layer is denoted by layer 2 and layer 5, respectively.

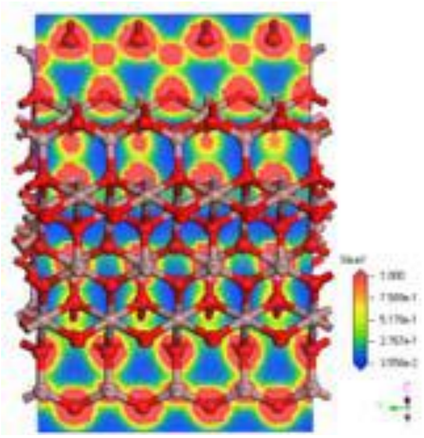
Optimized atoms	Formation energy (eV) Layer 2	Layer 5
Ignoring relaxation	9.35	9.90
11 layers(5 full opt+6 Zopt)	8.98	9.68
11 layers (full opt)	8.97	9.64
11 layers (full opt)+dipole correction	8.91	9.53

Same calculation is repeated for Ga2O3, the interest here si to compare the behavior of the material with alumina and Indium oxide. We have shown a simpler HOMO trend for Ga and the distribution looks very uniform without defect.

Ga_2O_3



Chosen HOMO



Electron density

We consider the energy formation of Al vacancies in the bulk and in the Al-terminated surface for super cell with 560 atoms. All calculations were performed with TSUBAME 16 cores.

For the unrelaxed alpha-alumina, the cost to remove a neutral Al atom is of 16.83 eV, allowing the 6 nearest anions to relax drops this energy to 15.91 eV. Further relaxation up to 16, 58, or 89 atoms around the Al vacancy has only a minor effect since the energy formation decreases to 15.63, 15.51, and 15.49 eV, respectively. As in the case of the oxygen vacancy, the larger relaxation effect occurs for the nearest-neighbor ions, which in this case relax roughly by 7%–8% ~Table 2. However, for the bulk neutral Al vacancy, the second nearest-neighbor relaxation is also significant, 4%. In the case of the surface Al vacancy, the energy formation for the unrelaxed substrate, calculated with respect to the corresponding relaxed clean surface, is 14.95 eV.

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まとめ、今後の課題

We have performed the defect concentration variation for Alumina with 2, 4 and 6 Oxygen vacancy per 560 atoms. This is to compare the formation energy of the vacancy and its relative stability, with that result the next step will be to see the adsorption of metal cluster to see the stability and hence the catalytic activity. With Ga_2O_3 and InO_2 the initial structure optimization with their relate properties were calculated we wish to do the similar concentration of vacancy concentration study with these tow oxides followed by the adsorption energy of related metal clusters to correlate the activity.

The aluminum vacancy results is very new in terms of vacancy concentration and we need to perform the adsorption energy calculation or and the vacancy formation energy for other TM oxides.

This work has been done by Abhijit Chatterjee, Principal Scientist of Accelrys K.K.