Surface Science 605 (2011) 1473–1479

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/ locate/susc

Theoretical study of the (110) surface of $Sn_{1-x}Ti_xO_2$ solid solutions with different distribution and content of Ti

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ARTICLE INFO

Article history:
Received 4 March 2011
Accepted 13 May 2011
Available online 20 May 2011

Keywords:
Density functional calculations
Tin oxides
Titanium oxide
Surface relaxation and reconstruction
Surface energy
Low index single crystal surfaces
Semiconducting surfaces
Surface structure morphology

ABSTRACT

The composition and thermodynamic stability of the (110) surface of $Sn_{1-x}Ti_xO_2$ rutile solid solutions was investigated as a function of Ti-distribution and content up to the formation of a full TiO_2 surface monolayer. The bulk and (110) surface properties of $Sn_{1-x}Ti_xO_2$ were compared to that of the pure SnO_2 and TiO_2 crystal. A large supercell of 720 atoms and a localized basis set based on the Gaussian and plane wave scheme allowed the investigation of very low Ti-content and symmetry. For the bulk, optimization of the crystal structure confirmed that up to a Ti-content of 3.3 at.%, the lattice parameters (*a*, *c*) of SnO_2 do not change. Increasing further the Ti-content decreased both lattice parameters down to those of TiO_2. The surface energy of these solid solutions did not change for Ti-substitution in the bulk of up to 20 at.%. In contrast, substitution in the surface layer rapidly decreased the surface energy from 0.99 to 0.74 J/m^2 with increasing Ti-content from 0 to 20 at.%. As a result, systems with Ti atoms distributed in the surface (surface enrichment) had always lower energies and thus were thermodynamically more favorable than those with Ti homogeneously distributed in the bulk. This was attributed to the lower energy necessary to break the Ti–O bonds than Sn–O bonds in the surface layer. In fact, distributing the Ti atoms homogeneously or segregated in the (110) surface led to the same surface energy indicating that restructuring of the surface bond lengths has minimal impact on thermodynamic stability of these rutile systems. As a result, a first theoretical prediction of the composition of $Sn_{1-x}Ti_xO_2$ solid solutions is proposed.

1. Introduction

Several industrially and scientifically important wide band gap semiconductors, such as SnO_2 and TiO_2, have a rutile structure at room temperature. Tin oxide is a key component for chemo-resistive gas sensors [1,2], solar cells (as transparent conductive oxide) [3,4] and catalysts [5,6]. Titanium oxide has found great application as white pigment [7], UV-absorber [8] and photo-catalyst [7]. $Sn_{1-x}Ti_xO_2$ solid solutions with rutile crystal structure have demonstrated unique properties with remarkable potential in several applications. More specifically, the photo-catalytic activity of TiO_2 nanoparticles was enhanced by formation of substitutional solid solution with Sn [9–11]. The distribution of the heteroatom was found to affect catalyst deactivation [12]. More recently Sn-doped TiO_2 was found to exhibit enhanced visible region photocatalytic activity as compared with undoped material in dye degradation experiments [12]. The improved performance was attributed to narrowing of the bulk band gap at low doping levels coupled with the introduction of surface states associated with segregated Sn ions in divalent state. Similarly, the gas sensing performance of SnO_2 nanoparticles, the most widely used sensing oxide, was remarkably improved by Ti doping at low content [13]. In particular, the cross-sensitivity to humidity (a major drawback) of SnO_2-based gas sensors was minimized by Ti-doping at $x = 4.6$ at.% content [13]. This is a key step toward the application of chemoresistive gas sensors in breath analysis and thus to non-invasive medical diagnostics as water vapor is omnipresent in the breath. Application of Ti-doping to other important gas sensing metal oxides requires further understanding of the resulting surface composition and chemical properties.

However, the determination of the surface composition of $Sn_{1-x}Ti_xO_2$ solid solutions and especially of such nanoparticles is still not very advanced. In fact, the spatial distribution of the dopant in the host lattice greatly affects the material's performance and its experimental determination is a challenging and demanding task for nanoparticles. Theoretical investigations may therefore greatly help and pave the way towards a rational design of novel nanomaterials with enhanced performance and optimal composition.

In contrast to pure SnO_2 and TiO_2 crystals, the composition of the rutile $Sn_{1-x}Ti_xO_2$ surface has been barely investigated yet. Density functional theory (DFT) studies have been performed for bulk

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doi:10.1016/j.susc.2011.05.016

$Sn_{1-x}Ti_xO_2$ [14] and for very limited contents of Ti-doped SnO_2 [15] and Sn-doped TiO_2 [16], investigating surface relaxation upon substitution on five- or six-fold metal sites. Both for SnO_2 [17] and TiO_2 [18], the (110) surface is the thermodynamically most stable and active plane with respect to gas sensing. The computed surface energy (0.53 J/m^2) [19] for rutile (110) TiO_2 is considerably lower than that (1.03 J/m^2) [19] of rutile (110) SnO_2. Studies on substitutional doping of the rutile SnO_2 (110) surface have shown that six-fold metal sites are preferred for substitution in the case of Ru-doping [20], whereas five-fold sites were preferred for Pd-doping [21].

Oxide surfaces have often been simulated effectively by density functional theory using the plane-wave formalism with small supercells at k-points convergence [15,16,20–23]. However, this limited the minimal surface and total doping content to relatively high values, such as 25 at.% and 8.3 at.% [15], respectively. Furthermore, symmetric and uniform impurity distributions are forced due to the application of periodic boundary conditions [14] in comparison to the real materials. To investigate the properties of $Sn_{1-x}Ti_xO_2$ solid solutions with low Ti-contents (≤4.6 at.%), relatively large supercells are required and thus more size efficient formalisms such as mixed Gaussian and plane wave (GPW) are necessary [24,25]. In fact, the application of the GPW scheme to solve the Kohn–Sham equations allows investigation of metal oxides with several hundreds of atoms with high efficiency [26]. The use of approximated local (Local Density Approximation, LDA) and semilocal (Generalized Gradient Approximation, GGA) exchange-correlation potentials in DFT limits the accuracy of the calculations. This is in particular apparent in the band gap energy of semiconducting materials which can differ remarkably from experimental results [27–29], leading, for example, to the incorrect prediction of a metallic character of Ge [30]. However, LDA and GGA are known to well predict ground-state properties, such as lattice parameters, surface geometrical displacements, surface energy and adsorption properties [31]. The use of hybrid functionals improves the calculations of band gaps for some semiconductors. However, hybrid functionals are computationally more demanding than LDA or GGA and sometimes less accurate than GGA functionals, for example in the prediction of cohesive energies of metals [31].

Here, DFT calculations based on the GPW method [24,25] were used to determine the lattice parameters and adsorption properties of ideal (without defects) rutile $Sn_{1-x}Ti_xO_2$ (110) surfaces as a function of the Ti-distribution. In this way, it was possible to investigate the properties of highly asymmetric systems from high to very low Ti-content (x = 1.3 at.%). Three types of Ti atom distributions were investigated: i) homogeneous Ti-distribution in the bulk, ii) homogeneous distribution in the surface layer, and iii) segregated distribution in the surface layer. The restructuring of the surface was quantified by the structural changes of the metal and oxygen atoms in the surface with respect to the bulk. The thermodynamic stability of the resulting crystals was evaluated based on their surface energy.

2. Methods

The DFT computations were performed with the CP2K program package, a suite of programs aimed at performing efficient electronic structure calculations and molecular dynamics [32]. The GPW formalism was utilized for the calculations of the electronic structure [24,25] at the Γ point. The interaction of valence electrons with frozen atomic cores was described using norm conserving, dual-space type pseudopotentials [33]. For Sn and Ti metal atoms, 4 and 12 electrons, respectively, were explicitly considered in the valence shell. A double-zeta valence with polarization (DZVP) basis set, optimized according to the Mol-Opt method [34], was adopted for the metal atoms (S5). For O atoms, 6 valence electrons were considered and a triple-zeta valence basis set with polarization (TZVP) was used (S5). For auxiliary PW expansion of the charge density, an energy cutoff of 400 Ry was necessary to achieve the energy convergence in the reciprocal space. Exchange-correlation potentials with general gradient approximation were modeled using the Perdew–Burke–Ernzerhof (PBE) functional [35]. This exchange-correlation potential has been shown to give results for rutile type structures in good agreement with experimental data [36].

The bulk supercell was obtained by multiplication of the orthorhombic rutile primitive cell (Fig. 1, inset) in all spatial directions. Convergence of the wave function was reached with 3, 4 and 10 unit cells in the x, y and z direction, respectively. This expansion roughly corresponds to the use of an unshifted (3 × 4 × 10) k-points grid. The resulting supercell consisted of 720 atoms (240 metal atoms and 480 oxygen atoms). All simulations were performed with periodic boundary conditions. Determination of the optimal lattice parameters *a, c* and *u* (Table 1) was carried out by self-consistent wave function calculations for different lattice values until the convergence in the total energy was lower than 10^{-3} eV per metal atom of the supercell. The optimization of the lattice parameters was done for different cell sizes (96, 216 and 720 atoms) (S1). For pure SnO_2, the lattice constant *a* increased from 4.80 to 4.86 Å, while *c* decreased from 3.32 to 3.28 Å with increasing cell size from 96 to 720 atoms. To determine the total energy of the bulk, all atom positions were allowed to relax starting from the optimal lattice parameters.

Surface calculations were performed using the supercell optimized for bulk calculations. In addition, 20 Å of vacuum were added along the z-direction in order to avoid any interaction of the slab with its periodic images. The surface explicitly contained 60 atoms (including bridging oxygen atoms), 24 of which were metallic. Five metal atom layers are sufficient for simulation of the (110) SnO_2 surface [37–39]. Here, 10 layers were used to obtain convergence of the system's

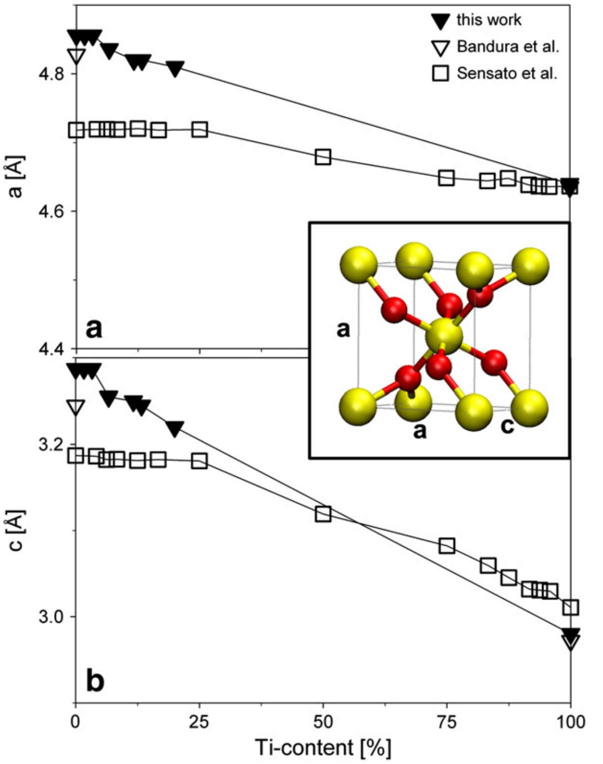

Fig. 1. Lattice parameters *a* (a) and *c* (b) of rutile $Sn_{1-x}Ti_xO_2$ solid solutions as computed here (filled triangles) using the PBE exchange-correlation functional in comparison with previous computational studies using the PBE (Bandura et al. [19], open triangles) and the hybrid B3LYP (Sensato et al. [14], squares) functional. All DFT calculations were within ± 3% of each other. The lattice parameters decreased from those of pure SnO_2 to those of pure TiO_2 showing slight deviations from Vegard's law (Table 1). The inset shows the unit cell of rutile SnO_2 (Sn = yellow, O = red), space group $P4_2mnm$.