Carbon at the Ti site in strontium titanate from first principles

Mead S AL-Hadidi, J P Goss, P R Briddon, Raied A Al-Hamadany and Mariam E Ahmed
Electrical and Electronic Engineering, Newcastle University, Newcastle upon Tyne, UK
E-mail: m.al-hadidi@ncl.ac.uk

Abstract. Perovskite oxides have attracted both experimental and theoretical attention due to their high permittivities, with SrTiO$_3$ used in waveguides, high capacity computer memory cells and dielectrics. Different growth methods yield various qualities of material, and thin-films growth using organic precursors makes carbon contamination highly probable. Using density functional theory we have calculated the electronic structure and vibrational properties of carbon substituting for Ti in cubic SrTiO$_3$. We find a relatively modest impact upon the electronic structure, with predicted impact upon observable factors, particularly the vibrational spectra and dielectric constant.

1. Introduction
ABO$_3$ perovskites have been widely studied for use in optoelectronics[1], ferroelectric[2, 3, 4], waveguides[1], high capacity computer memory cells[5, 1] and dielectrics[1]. Indeed, a major challenge in the semiconductor industry is to find suitable high-κ dielectrics to replace the SiO$_2$ in micro- and nano-electronic devices. To this end, materials including TiO$_2$, HfO$_2$ and the perovskite titanates SrTiO$_3$ and BaTiO$_3$ have been highlighted[6, 7]. Bulk crystalline SrTiO$_3$ has a relative permittivity of hundreds at room temperature, making it highly suitable for nano-size devices[8]. However, in thin films leakage current is a major issue, with native point defects, crystallinity and impurities remaining a significant problem.

Different deposition methods have been used to grow SrTiO$_3$ thin films, including chemical vapour deposition[9], molecular beam epitaxy[10] and pulsed laser deposition[11]. Recently, atomic layer deposition, sometimes referred to as atomic layer epitaxy, has attracted more attention due to its accurate thickness control and superior conformal growth[12, 13]. However, the organic Sr precursors lead to contamination[14, 15], and of particular note, carbon impurities have been reported in SrO and SrTiO$_3$ films[16]. In the case of SrO films, the current understanding of carbon contamination[17] is the formation of SrCO$_3$ within the SrO, and the appearance of the carbon contamination may be viewed as an incompleteness of the growth reactions[14].

There are many first principles simulation studies focusing on the electronic properties of impurities in SrTiO$_3$, but relatively few of them relate to carbon. In one density functional simulation[18], carbon is assumed to lie on an oxygen site, where it was found to generate a mid-gap 2p atomic orbital like, partially occupied state. Another study compared different sites, and suggested that the Ti site is more favourable[19], where it was proposed to introduce...
an empty band a little below the host conduction band minimum. However, the comparison in this study examines formation energies where the growth conditions differ with the substitution site, so it is difficult to draw an absolute conclusion from this data.

In this paper, we present the results of first principles calculations on the geometry, electronic structure, vibrational modes and reorientation barrier of carbon substituting for Ti in SrTiO$_3$.

2. Computational details

The properties of carbon substituting for Ti in SrTiO$_3$ are calculated using first-principles density functional theory within the local density approximation[20], as implement in the AIMPRO computer code[21, 22].

Atoms are modelled using norm-conserving, separable pseudo potentials[23] (the valance sets of Sr, Ti, O and C are 4s$^2$4p$^6$5s$^2$, 3s$^2$3p$^6$3d$^2$4s$^2$, 2s$^2$2p$^4$ and 2s$^2$2p$^2$, respectively) and the Kohn-Sham eigen-functions are expanded using atom centred Gaussian basis sets[24]. The bases consist of independent sets of s-, p- and d-type Cartesian Gaussian functions of four widths yielding 40 functions per atom for Ti, O and C, while five width of s- and p-Gaussians, yielding 20 functions per atom, centred at Sr. Matrix elements of the Hamiltonian are determined using a plane-wave expansion of the density and Kohn-Sham potential[25] with a cut-off of 150 Ha, resulting in absolute convergence of the total energy with respect to the expansion of the charge density to better than 10 meV.

Structures are optimised using a conjugate gradients scheme, with the optimised structures having forces of $< 10^{-3}$ atomic units and the final structural optimisation step is required to result in a reduction in the total energy of less than $10^{-5}$ Ha. Although SrTiO$_3$ has an ideal cubic perovskite type structure at room temperature, with the Ti$^{+4}$ ions being six fold coordinated to O$^{-2}$ ions, and each Sr$^{+2}$ surrounded by four TiO$_6$ octahedron, at very low temperatures, SrTiO$_3$ undergoes[26] a small antiferroelectric distortion with alternate TiO$_6$ groups rotating about a [001] axis in opposite senses by 1.89$^\circ$. The low-temperature structure is reproduced in the current computational approach, both in terms of the angle of distortion and the associated energy[27]. For bulk cubic SrTiO$_3$, our computational approach yields an equilibrium lattice parameter of 3.87 Å, within 1% of experiment[28]. The calculated band-gap is 1.85 eV, reflecting the well documented underestimate arising from the underpinning methodology. Our estimate is consistent with previous comparable calculations[29, 30].

To model the defect, we use the standard supercell approximation. In particular, a non-primitive supercell with lattice vectors 2[aa\bar{a}], 2[\bar{a}a\bar{a}] and 2[\bar{a}\bar{a}\bar{a}] is used, where a is the lattice constant in the cubic unit cell. This supercell is comprised from 32 formula units, meaning the supercell is Sr$_{32}$Ti$_{32}$O$_{96}$. In all cases the Brillouin zone is sampled using uniform $2 \times 2 \times 2$ Monkhorst-Pack mesh[31].

Vibrational modes have been calculated by obtaining the second derivatives of the energy with respect to atomic positions, which are then assembled into the dynamical matrix. The second derivatives are obtained from a finite difference approximation involving the forces calculated on atom $i$ when displacing atom $j$ in each of the three Cartesian directions. As such, they include even anharmonic terms in the vibrational potential, and the resulting vibrational modes are termed quasi-harmonic. From the dynamical matrix the eigen values yield the squares of the vibrational frequencies and eigen vectors the normal coordinates.

Finally, for activation energies the climbing nudged elastic band method has been used[32, 33], and the convergence of the saddle point energy with respect to the number of images and the image-forces has been established to within a few meV.
3. Results and discussion

3.1. Defect geometry

The substitution of titanium by carbon, C\textsubscript{Ti}, may be anticipated on the grounds of both C and Ti being group-IV elements. We have optimised a configuration where the initial structure has been perturbed from the ideal octahedral symmetry, avoiding any artificial symmetry constraint. We find that the relaxed structure has three C–O bonds significantly shorter (1.29 Å) than the Ti–O inter-nuclear distances in SrTiO\textsubscript{3} (1.93 Å). The calculated C–O bond-lengths in C\textsubscript{Ti} are close to those of the carbonate group\cite{34, 35}, so that the relaxation of the structure into the highly distorted geometry can be interpreted in terms of formation of a carbonate ion, CO\textsubscript{3}\textsuperscript{2–}, associated with a single Sr\textsuperscript{+2} cation. The structure is shown schematically in figure 1, and after structural optimisation we find it to have very close to C\textsubscript{3v} symmetry. Here, carbon forms covalent bonds with three of its O neighbours, leaving three of oxygen ions effectively under co-ordinated, but overall the anions and cations are balanced. For the simulation supercell, (SrTiO\textsubscript{3})\textsubscript{32}, one might express the substitution of Ti by C as resulting in (SrTiO\textsubscript{3})\textsubscript{31}(SrCO\textsubscript{3})\textsubscript{1}, or approximately (SrTiO\textsubscript{3})\textsubscript{0.97} (SrCO\textsubscript{3})\textsubscript{0.03}.

Figure 1. Schematic of (b) C\textsubscript{Ti} in SrTiO\textsubscript{3}, with an equivalent section of defect free SrTiO\textsubscript{3} shown in (a) for comparison. Green, grey, red and black atoms represent Sr, Ti, O and C respectively. Vertical and horizontal axes are approximately [001] and [010], respectively, with the tilted view adopted to aid clarity.

We now turn to the impact that the formation of the carbonate group has upon the electronic properties of the material.

3.2. Electronic structure

The calculated electron band structure for C\textsubscript{Ti} superimposed upon the band edges of pure SrTiO\textsubscript{3} is shown in figure 2. We first note that the inclusion of carbon has the apparent effect of increasing the band-gap. In fact, the extent of the increase in band gap is found to depend upon the effective concentration of C, with the increase larger where C\textsubscript{Ti} is modelled in a smaller simulation cell. This is to be expected as the band gap of pure SrTiO\textsubscript{3}, at 3.25 eV, is smaller than that of Sr(CO\textsubscript{3}) at around 4.3 eV\cite{36}, so the 1% alloy might well be expected to have a band gap slightly larger than pure SrTiO\textsubscript{3}.

In addition to the calculation of the band structure, preliminary calculations for the static dielectric function suggest a reduction in the presence of C\textsubscript{Ti}, consistent with the increase in the band-gap. We find that the electronic part of the static dielectric function\cite{30} is reduced by around 7% for a C:Ti ratio of 1:31.
3.3. Vibrational modes
To provide a mechanism for direct identification of $\text{CTi}$ in experiment, a local vibrational mode above the one-phonon maximum could prove highly effective. Of particular note, for the $C_{3v}$ $\text{CTi}$ centre we found a degenerate ($E$) C–O stretch mode at 1414 cm$^{-1}$, and a breathing stretch-mode with $A_1$ symmetry at 1081 cm$^{-1}$. These are close to the values of the $D_{3h}$ carbonate group [37] which have $E'$ and $A_1'$ stretch modes lying around 1415 cm$^{-1}$ and 1064 cm$^{-1}$, respectively. Lower frequency modes of the carbonate group are also present for $\text{CTi}$, but are resonant with the one-phonon density of states. Both of the local modes are infra-red and Raman active, and given sufficient concentrations one might seek to confirm the presence of this form of carbon centre directly via either IR or Raman spectroscopy.

3.4. Carbonate group reorientation
Finally, we have examined the energetics for reorientation of the carbonate group. The initial and final structures, and the energy profile along the minimum energy path between them, are shown in figure 3. The activation energy for reorientation is predicted to be around 2.5 eV. This relatively high value is a consequence of the covalent bonding within the carbonate group, so that reorientation involves both the breaking and formation of strong chemical bonds. The carbonate group may be oriented with the principle axis along any of the eight $\langle 111 \rangle$ directions if randomly orientated. However, under specific conditions, such as (111) biaxial strain induced by interface mismatch, the different orientations would have different energies, and given the high energy for reorientation, may be preferentially aligned. Since the $\text{CTi}$ structure has a permanent electric dipole, a polarised population of defect centres that are unable to reorient under normal temperature and electric field conditions, would be expected to have an impact upon the dielectric anisotropy and, where ferroelectric distortions are induced under strain, $\text{CTi}$ would be expected to alter both the details of the phase, and the resulting dielectric constant.

4. Summary and conclusions
In summary, we have studied the geometry, electronic structure and vibration modes for a C impurity substituting for titanium in cubic $\text{SrTiO}_3$ using first principles calculations. We find that $\text{CTi}$ represents the formation of carbonate groups, supported by both the geometry of the optimised structure and the calculated vibrational modes for this defect. Furthermore, by
Figure 3. Schematic of (a) initial, and (b) final structure of C$_{Ti}$ in SrTiO$_3$ in a simple reorientation process. Colours and orientation are as indicated in figure 1. (c) Calculated reorientation barrier of C$_{Ti}$ in SrTiO$_3$ between initial and final structure.

comparison between the band structure for pure SrTiO$_3$ and the impurity system, carbon in this form does not directly change the conduction electron or hole concentrations of the system by doping, but by an increase in the band-gap in high carbon concentration materials the thermally generated concentration of carriers is expected to be reduced. Therefore, C$_{Ti}$ is predicted to have a modest impact upon the electrical conductivity of SrTiO$_3$ at high concentrations, and is not responsible for an increase in leakage current in capacitive device elements. Finally, we also estimated the reorientation barrier for the carbonate group, and because the process involves the breaking of C–O covalent bonds, the barrier is a relatively high value at around 2.5 eV. Such a barrier when combined with the fact that C$_{Ti}$ has a permanent electric dipole is anticipated to have an impact upon the dielectric properties of SrTiO$_3$ in an alternating electric field.

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