A quantum mechanical study of the stability of SnO_2 nanocrystalline grains

A quantum mechanical study of the stability of SnO_2 nanocrystalline grains

A M Mazzone

CNR, Istituto IMM-sez.di Bologna-via Gobetti 101, Bologna-40129, Italy

E-mail: mazzone@lamel.bo.cnr.it.

Abstract
The purpose of this study is to gain insight into the instability which is observed, under operative conditions, in SnO_2 nanocrystalline materials. To this end, the binding and fragmentation energies of SnO_2 crystalline grains have been evaluated quantum mechanically at the semi-empirical level using the extended Debye–Hückel approximation. The size and shape of the grains, whose lattice has a rutile structure, are variable and a parametric search has been carried out on both quantities. The main result of this study is that the oxygen content, which depends on the grain structure, has a critical effect on its stability. This finding is supported by calculations for small homonuclear clusters formed by oxygen and tin.

1. Introduction

It is known that nanocrystalline materials consist of two main components, i.e. a grain component formed by crystalline clusters with nanometre dimensions and an interface component formed by large interfaces and surfaces. The focus of the current research is on this latter and the aim of these studies is to elicit similarities and differences as regards the bulk behaviour. However, many problems observed when using nanocrystalline materials suggest that a careful study of the grains is also needed. A notable example is offered by SnO_2. In fact, SnO_2 nanocrystalline structures have found important applications and numerous current experimental studies are dedicated to this material [1, 2]. However, its practical exploitation is limited by the instability of its performance in long operations at near room temperature and, among other explanations, the effect has been attributed to the poor stability of the grains [3]. A subtle question is whether this instability arises from a known defect of the bulk state, such as faulty stoichiometry, or is due to the finite size of the grain. Addressing this point is the aim of this study. The approach adopted to this end consists in the evaluation of the grain total energy E_t which is carried out quantum mechanically at the semi-empirical level using the extended Debye–Hückel approximation (EHA). The grain structures used in these calculations
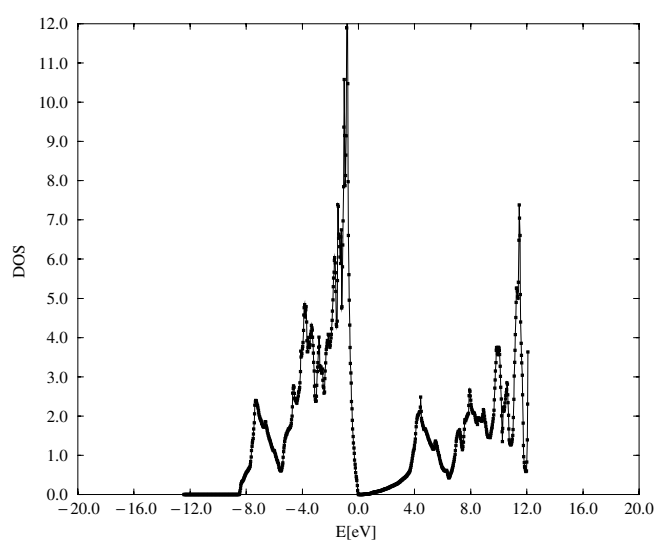
Figure 1. The DOS of SnO_2 with the rutile structure.

compare realistically with the experimental ones and the grain size, shape and composition are variable. From the functional dependence of E_t on these parameters we deduce their effects on the grain stability.

The plan of the work is as follows. In section 2 we give some details on the calculation methods. Section 3 is miscellaneous. It illustrates properties of crystalline SnO_2 and of small tin and oxygen clusters. These last calculations are carried out using the EHA and LDA. Therefore, in addition to an introduction to the properties of grains, they offer qualitative insight into the validity of the EHA. The properties of the nanocrystalline grains are presented in section 4.

2. Computational details

As mentioned in the introduction, the simulation method consists in a parametric search for minima of the total energy E_t. In the cluster literature, this search is commonly carried out starting from families of structures chosen on the basis of a plausible physical behaviour. Device studies [4] indicate that, depending on the preparation techniques, nanocrystalline films are columnar or spongy with a spherical shape. The grain dimensions are in the range from 3 to 20 nm. Accordingly, two basic models of grains, i.e. columnar (C) and spherical (S), have been used in the simulation. In the case of columnar structures the column section is squared, rectangular (both indicated by C), L-shaped (L), or geminate (G)—that is, formed by two adjoined columnar grains. In all cases the grain lattice retains the rutile structure of the bulk material. The grain size N varies from 20 to 400 atoms with the linear dimension in the range from 0.3 to 4 nm. The ratio X_M/X_O between the tin (metal) and the oxygen content falls in the range between 0.4 and 0.6.

Early studies on solids with a rutile lattice were carried out at the semi-empirical level using the EHA [5, 6]. This simple approach allowed a correct systematization of the energetics of these elements over a wide range of structural parameters. More recent calculations adopt the LDA with a variety of formulations to solve the Kohn–Sham equations (see [7, 8] and references therein). In this study three methods, i.e. the EHA, LDA and FPLAPW, have been
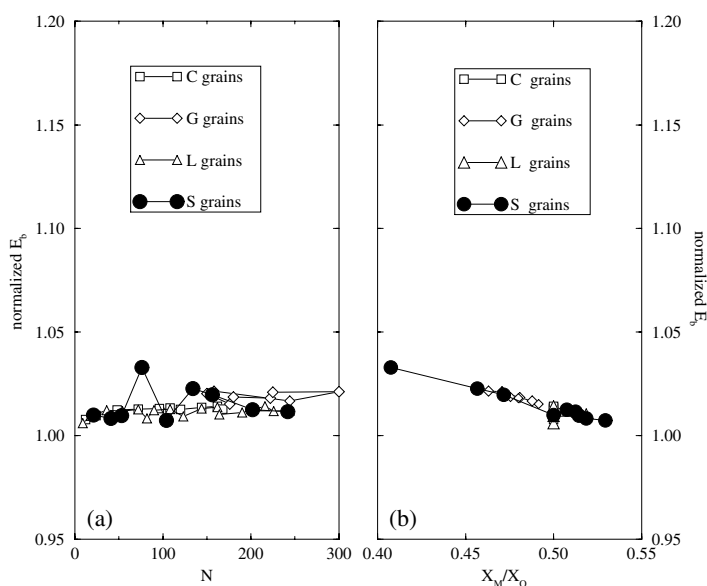
Figure 2. The binding energy as a function of the size (a) and of the stoichiometry (b).

adopted. The EHA has been applied to the large grain structures described above. As a test of the validity of these calculations, EHA calculations for small oxygen and tin clusters have been compared with LDA. The FPLAPW method has been adopted for the evaluation of the density of states (DOS) of crystalline SnO_2, reported in section 3. A detailed description of the three methods can be found in [9]. Here it is only mentioned that FPLAPW and LDA calculations are based on the methods implemented in the packages WIEN97 [10] and DeFT [11], respectively. DeFT uses the Vosko–Wilk–Nusair local spin density functional with the Becke–Perdew gradient-corrected correlation functional, which is also used in WIEN97. QCPE software [12] has been adopted for the EHA calculations.

In the physico-chemical literature the stability of a clustered structure is evaluated from the binding energy E_b which is the energy needed to bring the atoms into the clustered form from an assembly of free atoms. In elasticity studies the stability of a solid structure is evaluated from a 'fragmentation energy' E_f which represents the energy cost of cutting the crystal along a major direction. While E_b offers a simple picture of the quality of bonding in the whole structure, E_f describes the stability of the inner parts of the grains. In our study both E_b and E_f have been used. In figure 2 E_b is measured with respect to the binding energy of a SnO_2 unit with a rutile lattice. This presentation offers the advantage of allowing an immediate comparison with the bulk where the value of the normalized E_b is 1. In figure 3 E_f is obtained by cutting the grain into two symmetric pieces and is measured as the decrease of E_b in the two pieces.

3. The properties of crystalline SnO₂ and of small tin and oxygen clusters

FPLAPW calculations of the DOS of crystalline SnO_2 are reported in figure 1. The figure shows the partial DOS obtained by decomposing the charge according to the contributions of oxygen and tin atoms. The lowest-energy bands (partially shown in figure 1) correspond to O 2s states. The peak under the Fermi energy (which is at -10 eV in the plot) derives mainly from O 2p states, with some contribution from Sn 5s orbitals, and the charge above the Fermi
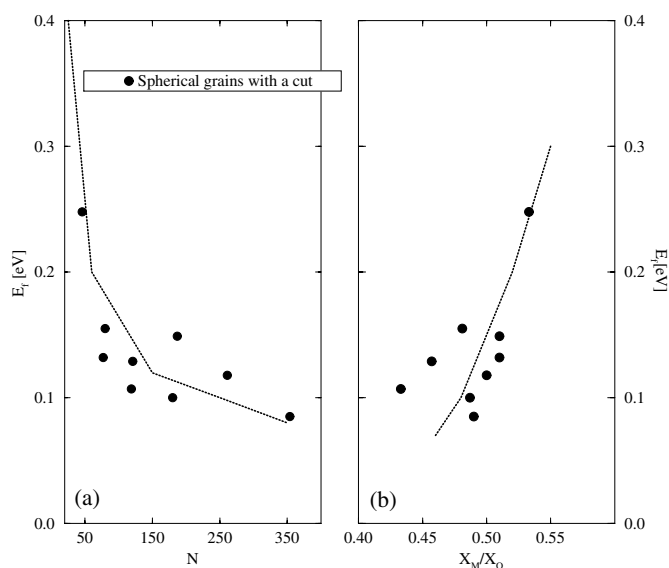
Figure 3. The fragmentation energy as a function of the size (a) and of the stoichiometry (b).

energy arises from Sn 5p states. The DOS plot clearly shows the composite nature of the bonding in SnO_2. In fact, the separation of O 2p and Sn 5p across the Fermi energy is broadly in line with a simple ionic model with two independent lattices formed by tin and oxygen. However, the admixture of O 2p and Sn 5s indicates also a high degree of covalency and the gap across the Fermi energy shows a semiconductor behaviour.

The binding properties of oxygen and tin clusters with size $N \leqslant 4$ are illustrated in table 1. The notable aspects of these calculations are two. First, from the computational side, there is an evident difficulty in the evaluation of bonding in oxygen-based clusters and materials. In fact, LMTO-LDA calculations of O_2, taken from the literature [13], give an overbinding of at least 1.2 eV/atom with respect to experiments. The methods adopted in this study offer a perceptible improvement over these early calculations. For O_2 and Sn_2 the values of E_b and of the bond length are acceptably close to the experimental values and the structure of O_4 obtained using the EHA consists of two O_2 clusters which, is in agreement with experiments. Furthermore, E_b approximately follows the same size dependence in EHA and DeFT and the differences between E_b and the bond length in the two calculations oscillate between 0.1 and 0.3 eV and 0.1 and 0.6 Å, respectively. These differences are acceptable, if one considers the state of the art in cluster calculations. Secondly, from a physical point of view, the properties of these small structures offer useful insight into possible differences between the crystalline SnO_2 and the grains of the same materials. In fact, the small size of the oxygen clusters, in comparison with that of tin clusters, suggests that compound clusters, even of a large size, retain the skeleton of the tin clusters. The oxygen cluster is simply embedded in this skeleton and the electronic structure of the compound structure derives from the separate contributions of the oxygen and tin subclusters. Also the electronic structure of the crystal indicates that the use of two separate sublattices is a reasonable approach. However, the large binding energy of O_2 (table 1), which is also the fundamental unit of the SnO_2 lattice, suggests that a slight increase of the oxygen content increases the electronic energy contribution. It therefore acts as a 'glue' and increases the cohesive strength of the lattice. The consequence of this feature for the grain stability will be examined in the following section.

Table 1. Homonuclear oxygen and tin clusters. Literature results and data obtained from EHA and DeFT calculations. The source of the experimental data, reported under the heading 'literature data', can be found in [9].

Cluster	Structure	Binding energy E_b (eV/atom)	Bond length (Å)
		Literature data	
O_2	—	−2.61, experimental	1.18, experimental
O_2	—	−3.83, −3.30, calculated [13]	1.20, calculated
Sn_2	—	−1.20, experimental	2.70
		EHA calculations	
O_2	—	−3.00	1.22
O_3	Triangle	−2.67	1.28
O_4	Two O_2 units	−3.01	1.22
Sn_2	—	−1.33	2.31
Sn_3	Triangle	−2.93	2.54
Sn_4	Rhombus	−3.61	2.67
		DeFT calculations	
O_2	—	−2.91	1.30
O_3	Triangle	−2.48	1.29
O_4	Linear	−2.55	1.20
Sn_2	—	−1.10	2.90
Sn_3	Triangle	−2.93	2.70
Sn_4	Rhombus	−3.33	2.92

4. The binding and fragmentation energies of SnO₂ grains

The effects of the grain size, geometry and composition on E_b and E_f are illustrated by figures 2 and 3. The size dependence of the normalized E_b shows a nearly flat asymptote of value 1, which is consistent with a bulk-like behaviour (figure 2(a)). However, in almost all cases there is a slight increase above 1 and an oscillatory behaviour is clearly observed for the S grains. These features are noticeable and are explained by figure 2(b). The figure shows E_b as a function of the ratio X_M/X_O between the number of metallic and oxygen atoms, for grains of all shapes. Perceptibly larger binding energies are observed in the oxygen-enriched structures, while a decrease of E_b is observed for the metal-enriched ones. The effect is a direct consequence of the large binding strength of the small oxygen units, illustrated in the previous section. Accordingly, the behaviour of E_b depends on whether the structural pattern in the grain family leads to a growth or to a reduction of the oxygen sublattice. In our calculations the grain structure is constructed without imposing any special constraint on the metal or oxygen content. The two quantities X_M and X_O vary freely with the grain size and shape and this leads to oscillations of the ratio X_M/X_O around the bulk value 0.5. The spread of the data points in figure 2(b) illustrates the extent of this effect in the various families of grains. While for C, G and L grains the spread is contained between 0.45 and 0.5, it ranges between 0.4 and 0.55 for the S grains. This large spread accounts for the larger oscillations of E_b observed in this family.

E_f quantifies the grain tendency to yield and, in principle, should exhibit the same size and composition dependence of E_b. In contrast, interesting differences between the two energies are observed. In fact, the size dependence of E_f (figure 3(a)) shows a perceptible decrease at the larger size. This indicates that the increase of the grain size increases its stability, which is not observed for E_b. Furthermore, as for E_b, the increase of the oxygen content (figure 3(b))

increases the grain stability. However, the comparison of figures 2(b) and 3(b) reveals that the dependence of E_b on X_M/X_O is sharper for E_f than for E_b.

5. Conclusions

The analysis performed on the dependence of E_b and E_f on the grain shape, size and composition has shown a primary dependence on the oxygen content. The comparison with small clusters shows that this effect is attributable to the large binding strength of oxygen clusters of minimal size and has therefore to be viewed as a property of the clustered state rather than a result of a defective composition in the solid. Furthermore, the dependence on the oxygen content may account for the observed instability if the operative conditions lead to a change of the cluster structure and composition. However, the difference in behaviour of E_b and E_f implies that a different grain response is to be expected under experimental conditions depending on which of the two energies controls the grain evolution.

References

[1] Wang D, Wen S, Chen J, Zhang S and Li F 1994 *Phys. Rev.* B **49** 14282
[2] Yu K M, Xiong Y, Liu Y and Xiong C 1997 *Phys. Rev.* B **66** 2666
[3] Dori L (EEC Project) 2000 *Clean Air Reports*
[4] Lalauze R, Breuil P and Pijolat C 1991 *Sensors Actuators* B **3** 175
[5] Grunes L A, Leapman R D, Wilker C N, Hoffmann R and Kunz A B 1982 *Phys. Rev.* B **25** 7157
[6] Burdett J K 1985 *Inorg. Chem.* **24** 2244
[7] Peltzer E L, Svane B A, Christensen N E, Rodriguez C O, Capannini O M and Moreno M S 1993 *Phys. Rev.* B **48** 15712
[8] Watson G W 2001 *J. Chem. Phys.* **114** 758
[9] Mazzone A M 2001 *Comput. Mater. Sci.* **21** 211
[10] Blaha P, Schwarz K and Luitz J 1999 *WIEN97, a Full Potential Linearized Augmented Plane Wave Package for Calculating Crystal Properties* Technical University of Vienna (ISBN 3-9501031-0-4)
 This is an improved and updated Unix version of the original copyrighted WIEN code, which was published by Blaha P, Schwarz K, Sorantin P and Trickey S B 1990 *Comput. Phys. Commun.* **59** 399
[11] St-Amant A, Cornell W D, Halgren T A and Kollman P A 1995 *J. Comput. Chem.* **16** 1483
[12] *QCPE* Program Number 571 (and references therein). Further information can be found at the Web site www.indiana.edu.
[13] Painter G S and Averill F W 1982 *Phys. Rev.* B **26** 1781