Electronic and magnetic properties of SnO$_2$/CrO$_2$ thin superlattices

Pablo D Borges$^{1*}$, Luísa MR Scolfaro$^2$, Horácio W Leite Alves$^3$, Eronides F da Silva Jr$^4$, Lucy VC Assali$^1$

**Abstract**

In this article, using first-principles electronic structure calculations within the spin density functional theory, alternated magnetic and non-magnetic layers of rutile-CrO$_2$ and rutile-SnO$_2$ respectively, in a (CrO$_2$)$_n$(SnO$_2$)$_n$ superlattice (SL) configuration, with $n$ being the number of monolayers which are considered equal to 1, 2, ..., 10 are studied. A half-metallic behavior is observed for the (CrO$_2$)$_n$(SnO$_2$)$_n$ SLs for all values of $n$. The ground state is found to be FM with a magnetic moment of 2 $\mu_B$ per chromium atom, and this result does not depend on the number of monolayers $n$. As the FM rutile-CrO$_2$ is unstable at ambient temperature, and known to be stabilized when on top of SnO$_2$, the authors suggest that (CrO$_2$)$_n$(SnO$_2$)$_n$ SLs may be applied to spintronic technologies since they provide efficient spin-polarized carriers.

**Introduction**

A variety of heterostructures have been studied for spintronics applications, and they have proved to have a great potential for high-performance spin-based electronics [1]. A key requirement in developing most devices based on spins is that the host material must be ferromagnetic (FM) above 300 K. In addition, it is necessary to have efficient spin-polarized carriers. One approach to achieve the spin injection is to create built-up superlattices (SLs) of alternating magnetic and non-magnetic materials. One attempt has already been made by Zaoui et al. [2], through ab initio electronic structure calculations for the one monolayer (ZnO)$_1$(CuO)$_1$ SL, with the aim of obtaining a half-metallic behavior material, since they are 100% spin polarized at the Fermi level and therefore appear ideal for a well-defined carrier spin injection.

In this study, the magnetic and electronic properties of (CrO$_2$)$_n$(SnO$_2$)$_n$ SLs with $n = 1, 2, ..., 10$ being the number of monolayers are investigated. These systems are good candidates to obtain a half-metallic behavior material since bulk rutile-CrO$_2$ has shown experimentally this behavior [3] and recently magnetic tunnel junctions based on CrO$_2$/SnO$_2$ epitaxial layers have been obtained [4].

**Theoretical method**

All the calculations were based on the spin density functional theory. The Projector-Augmented Wave method implemented in the Vienna Ab-initio Simulation Package (VASP-PAW) [5,6] was employed in this study, and for the exchange-correlation potential, the generalized gradient approximation and the Perdew, Burke, and Ernzerhof (GGA-PBE) approach was used [7]. The valence electronic distribution for the PAWs representing the atoms were Sn – 4$d^{10}$ 5$s^2$ 5$p^2$, Cr – 3$d^5$ 5$s^1$, and O -2$s^2$ 2$p^4$. Scalar relativistic effects were included. For simulation of the one monolayer (CrO$_2$)$_1$(SnO$_2$)$_1$ SL, a supercell with 12 atoms (2Sn, 2Cr, and 8O) in the rutile structure as shown in Figure 1a was used. For this case, a 4 × 4 × 3 mesh of Monkhorst-Pack $k$-points was used for integration in the SL BZ. All the calculations were done with a 490 eV energy cutoff in the plane-wave expansions.

**Results and discussion**

For the (CrO$_2$)$_1$(SnO$_2$)$_1$ SL, the calculation was started with the experimental lattice parameters of the tin dioxide, $a = 4.737$ Å, $c/a = 0.673$, and $u = 0.307$ [8-10]. The system was relaxed until the residual forces on the ions were less than 10 meV/Å. Good agreement between the calculated and the available experimental values for the lattice parameters is obtained, as seen in Table 1. Figure 1b shows that the ground state is ferromagnetic (FM), being the most stable state compared with the non-magnetic (NM) and anti-ferromagnetic (AFM) ones. For the
ground state, the total magnetic moment gives a value of 2 \( \mu_B \) per chromium atom. Figure 2a,b presents the total density of states (TDOS) and the projected density of states (PDOS), respectively for the Cr 3d orbital, showing that the system has a half metallic behavior, with the Cr 3d orbital appearing in the gap region, characterizing a metallic-like behavior for the majority spin and a semiconductor-like behavior for the minority spin. The band structures of the SL for spin up and spin down are depicted in Figure 2c. A band gap of approximately 1.71 eV is obtained for the minority spin at the \( \Gamma \)-point. There is a smaller gap for spin flip excitations from the Fermi level, which is approximately 0.86 eV. For the \((\text{SnO}_2)_n(\text{CrO}_2)_n\) SLs with \( n > 1 \), considered here up to \( n = 10 \), it was observed that the ground state remains as FM. The interplay of the \text{SnO}_2 and \text{CrO}_2 layer thicknesses does not change the half-metallic behavior, as can be verified through the DOS shown in Figure 3a,b for \( n = 10 \). The magnetic moment per Cr atom, in all the studied cases, is the same and equal to 2 \( \mu_B \). Moreover, the SL magnetization does not depend on the number of monolayers. This has been verified by performing calculations with one monolayer of \text{CrO}_2 grown between 3, 7, and 11 monolayers of \text{SnO}_2. It was observed that the SL magnetization remained equal to 2 \( \mu_B \). Our results show a 100% spin polarization at the Fermi level, ideal for a well-defined carrier spin injection.

An investigation, related to strain effects along the \( z \)-direction for the rutile phase of \text{CrO}_2, was made by simulating bulk rutile-CrO\textsubscript{2}, on top of tin dioxide, assuming for CrO\textsubscript{2} the lattice parameter \( a \) of SnO\textsubscript{2}, i.e., a situation in which the chromium dioxide is tensile. By varying the ratio \( c/a_{\text{SnO}_2} \) and minimizing the total energy of the system, the authors obtained the curves shown in Figure 4a for the FM, AFM, and NM states, showing that the transition from a FM to an AFM state occurs when \( c/a_{\text{SnO}_2} \) is about 0.544. At this value, a magnetic moment reduction is observed, as depicted in Figure 4b. These results suggest a magnetization change when the SL is under strain or, in other words, when \text{CrO}_2 is compressed. A similar behavior was found by Srivastava et al. for bulk rutile-CrO\textsubscript{2} under pressure \[11\].

The advantage in using the \text{SnO}_2/\text{CrO}_2 SLs, despite the fact that CrO\textsubscript{2} is unstable at room temperature, is that its stability becomes possible when grown on SnO\textsubscript{2} \[12\]. Our results showed that the interface effects due to the lattice mismatch do not change the chromium dioxide magnetism characteristics. If the distances between two planes perpendicular to the rutile \( c \)-axis containing the Cr\textsubscript{2} and Sn\textsubscript{1} are compared (see Figure 1a), at the interface region of the SL, before and after full

### Table 1

|       | \( a \) (Å) | \( c/a \) | \( u \) |
|-------|-------------|-----------|--------|
| \text{SnO}_2 | 4.737\textsuperscript{a} | 0.673\textsuperscript{a} | 0.307\textsuperscript{a} |
|        | 4.839\textsuperscript{b} | 0.670\textsuperscript{b} | 0.306\textsuperscript{b} |
| \text{CrO}_2 | 4.421\textsuperscript{c} | 0.6596\textsuperscript{c} | 0.301\textsuperscript{c} |
|        | 4.455\textsuperscript{d} | 0.6569\textsuperscript{d} | 0.304\textsuperscript{d} |
| \((\text{CrO}_2)_1(\text{SnO}_2)_1\) | 4.625\textsuperscript{a} | 0.658\textsuperscript{a} | - |
| \((\text{CrO}_2)_10(\text{SnO}_2)_10\) | 4.640\textsuperscript{a} | 0.6546\textsuperscript{a} | - |

\textsuperscript{a}[8]; \textsuperscript{b}[9]; \textsuperscript{c}[10]; \textsuperscript{d}this work.
Figure 2 Density of states and band structure for the (SnO$_2$)$_1$(CrO$_2$)$_1$ SL. (a) Total density of states (TDOS), (b) Project density of states (PDOS) for the Cr-3d orbital, (c) Band structure, for spin up and spin down, along the main symmetry lines of the SL BZ. The Fermi level, EF, is set to zero in (a), (b), and (c).

Figure 3 Density of states and total energies for the SL with $n=10$. (a) Total density of states (in black) and project density of states (in gray) for the Cr–3d. (b) Total energies for the non magnetic (NM) and anti-ferromagnetic (AFM) states relative to the ferromagnetic (FM) state. The Fermi level, EF, is set to zero. The dashed lines connecting the points are to guide the eyes.
relaxations, then changes of only approximately 4% are observed for all the studied SLs.

Conclusions
In conclusion, the results of first-principles electronic structure calculations, within the spin density functional theory, carried out for (CrO$_2$)$_n$(SnO$_2$)$_n$ SLs formed by alternating magnetic and non-magnetic layers of rutile-CrO$_2$ and rutile-SnO$_2$, where the number of monolayers $n$ was varied from 1 to 10, have been reported in this article. A half-metallic behavior is observed for all the studied (CrO$_2$)$_n$(SnO$_2$)$_n$ SLs. The ground state is FM, with a magnetic moment of 2 $\mu_B$ per chromium atom, which is independent of the number of monolayers. As the FM rutile-CrO$_2$ is unstable at ambient temperature, and known to be stabilized when on top of SnO$_2$, it is suggested that (CrO$_2$)$_n$(SnO$_2$)$_n$ SLs may be applied to spintronic technologies since they provide efficient spin-polarized carriers.

Abbreviations
AFM: anti-ferromagnetic; FM: ferromagnetic; GGA-PBE: generalized gradient approximation and the Perdew, Burke, and Ernzerhof; NM: non-magnetic; PDOS: projected density of states; SL: superlattice; TDOS: total density of states; VASP-PAW: Vienna Ab-initio Simulation Package and the Projected Augmented Wave.

Acknowledgements
The authors would like to thank the partial support from the Brazilian funding agencies FAPEMIG, FAPESP, CAPES, and CNPq, and from the Material, Science, Engineering and Commercialization Program at the Texas State University in San Marcos.

Author details
1 Instituto de Física, Universidade de São Paulo, CP 66318, São Paulo, SP, 05315-970, Brazil. 2 Department of Physics, Texas State University, San Marcos, TX, 78666, USA. 3 Universidade Federal de São João Del Rei, CP 110, São João Del Rei, MG, 36301-160, Brazil. 4 Departamento de Física, Universidade Federal de Pernambuco, Recife, PE, 50670-001, Brazil.

Authors’ contributions
PB performed the ab initio calculations, participated in the analysis, and drafted the manuscript. LS and PB conceived of the study. HA, ES, LA, and LS participated in the analysis and in the production of a final version of the manuscript. All authors read and approved the final manuscript.

Competing interests
The authors declare that they have no competing interests.

Received: 25 August 2010 Accepted: 15 February 2011
Published: 15 February 2011

References
1. Wolf SA, Awschalom DD, Buhrman RA, Daughton JM, von Molnár S, Roukes ML, Ch帖chelkanova AY, Treger DM: Spintronics: A Spin-Based Electronics Vision for the Future. Science 2001, 294:1488.
2. Zaoui A, Feihati M, Aghjia R. Magnetic properties of [ZnO01]/[CuO01] (001) superlattice. Appl Phys Lett 2009; 94:102102.
3. Anguelou A, Gupta A, Xiao Gang, Abraham DW, Ji Y, Ingvarsson S, Chien CL. Near-complete spin polarization in atomically-smooth chromium-dioxide epitaxial films prepared using a CVD liquid precursor. Phys Rev B 2001; 64:180408R.
4. Miao GX, LeClair P, Gupta A, Xiao G, Varela M, Pennycook S. Magnetic tunnel junctions based on CrO$_2$/SnO$_2$ epitaxial bilayers. Appl Phys Lett 2008; 93:023511.
5. Kresse G, Furthmuller J: Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput Mater Sci 1996, 6:15.

6. Kresse G, Furthmuller J: Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys Rev B 1996, 54:11169.

7. Perdew JP, Burke K, Ernzerhof M: Generalized Gradient Approximation Made Simple. Phys Rev Lett 1996, 77:3865.

8. Wyckoff R: In Crystal Structures. Volume 1. 2 edition. New York, London: John Wiley & Sons, 1963.

9. Borges PD, Scolfaro LMR, Leite Alves HW, da Silva EF Jr: DFT study of the electronic, vibrational, and optical properties of SnO2. Theor Chem Acc 2010, 126:39.

10. Maddox BR, Yoo CS, Kasinathan D, Pickett WE, Scalettar RT: High-pressure structure of half-metallic CrO2. Phys Rev B 2006, 73:144111.

11. Srivastava V, Sanyal SP, Rajagopalan M: First Principles study of pressure induced magnetic transition in CrO2. Indian J Pure Appl Phys 2008, 46:397.

12. Zabel H, Bader SD, (Eds): Magnetic Heterostructures: Advances and Perspectives in Spinstructures and Spintransport STMP 227 Berlin: Springer, 2008.

Cite this article as: Borges et al.: Electronic and magnetic properties of SnO2/CrO2 thin superlattices. Nanoscale Research Letters 2011 6:146.

doi:10.1186/1556-276X-6-146

Submit your manuscript to a SpringerOpen journal and benefit from:

► Convenient online submission
► Rigorous peer review
► Immediate publication on acceptance
► Open access: articles freely available online
► High visibility within the field
► Retaining the copyright to your article

Submit your next manuscript at ► springeropen.com