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Role of interface suboxide Si atoms on the electronic properties of Si/SiO_2 superlattices

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Abstract

Silicon/SiO_2 superlattices (SLs) are nanostructured thin films bearing multiple Si/SiO_2 interfaces. In such materials, silicon is walled by its oxide in order to generate multiple quantum wells. Here, the structural and electronic properties of a structurally-relaxed Si/SiO_2 SL model are studied using a first principles approach; the Si/SiO_2 interfaces contain all suboxide Si atoms (Si^{1+}, Si^{2+}, and Si^{3+}). The valence and conduction band offsets (VBO and CBO) are evaluated from the relative shift between densities of states (DOSs) of Si atoms in bulk SiO_2 and in the SL. The CBO is shown to be reduced compared to the VBO. The DOSs of the three suboxide Si atoms are also calculated. It is shown that there are contributions from all suboxides at the threshold of the gap.

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1. Introduction

Enhanced luminescence as well as blue shift with increased confinement in Si/SiO_2 superlattices (SLs) have been observed in several experiments [1]. In general, both the Si and the SiO_2 layers are amorphous. Recently, crystalline silicon (c-Si) wells, confined by the SiO_2 insulator walls, have been grown by Lu and Grozea [2], who report atomically sharp $SiO_2/Si/SiO_2$ interfaces. These 2D structures offer, over many other Si confined structures (such as quantum dots, wires, dislocation loops, etc.), the prominent advantage of high stability.

However, only few theoretical studies have been conducted in order to understand (and predict) the physical properties of these structured materials (see for instance [3] and reference therein). This is due in part to the amorphous nature of SiO_2 in the SLs, that requires large supercells to be correctly handled in the calculations. A collection of structurally-relaxed models, fully described in [3], have been constructed in order to evaluate the role of confinement and interfaces on the novel electronic and optical properties of Si/SiO_2 SLs. Their interface topology is formed by the three suboxide Si atoms, namely Si^{1+}, Si^{2+}, and Si^{3+}. The Si^0 and Si^{4+} atoms are ''bulklike'', respectively present inside the Si and SiO_2 layers of the SLs.

The density functional theory within the local density approximation (LDA) is used for the calculation

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of the electronic properties of the SLs. The Kohn–Sham equations [4] are solved via the projector-augmented waves numerical approach [5], a formal extension of the ultrasoft-pseudopotential method towards the linearized-augmented plane-waves all-electron method [6]. Full details are given in [3].

2. Results

In [3], it was shown that the Si/SiO_2 model structures have direct band gaps. A blue shift with increasing confinement was observed upon considering three different Si well thicknesses, namely 1.1, 1.7, and 2.2 nm. The enhancement of absorption due to the confinement of Si was also demonstrated. Furthermore, the oxygen atoms at the interfaces were shown to raise the energy gap and to increase the dispersion in the band structure near the Fermi level.

In the present article, we first estimate the valence band offset (VBO). It is obtained by comparing the mean value of the DOS of Si^{4+} atoms in the SL to that in the "ideal" beta-cristobalite SiO_2, symmetry group $I(\bar{4})2d$ (see for instance, Swainson and Dove [7] for a detailed discussion on "ideal" structures of SiO_2). In this structure, all Si–O bond lengths equal 1.61 Å, and all Si–O–Si bond angles are 147°, the same as for Si^{4+} in the SL models [3]; comparison of the electronic properties between this bulk SiO_2 structure and the SL is thus meaningful. The VBO is by definition the shift of the Fermi level between the two layers, i.e. respectively the Si^0 and Si^{4+} atoms in the SLs; the Fermi level in the SL is set according to the highest valence band, corresponding to Si^0 atoms in the well. Thus, the VBO can be evaluated by the difference between the lowest-lying peaks (near −20 eV) in the DOS for Si^{4+} atoms in the SL and in bulk SiO_2, both set according to their Fermi levels. This VBO equals 2.8 eV, as illustrated in Fig. 1(a). The LDA energy gap of c-SiO_2 and c-Si are respectively 5.6 and 0.6 eV, leading to a conduction band offset (CBO) of ∼2.5 eV ((5.6−0.6)/2), lower than the VBO (by 0.3 eV). However, it is well known that the LDA underestimates the energy gaps of semiconductors and insulators, and band offsets as well. By comparison, experimental energy gaps for c-SiO_2 and c-Si are respectively ∼9 and 1.1 eV, corresponding to VBO and CBO of the order of ∼3.95 eV ((9−1.1)/2). We thus infer from the present calculations that the CBO should be smaller than the VBO—by at least 0.3 eV.

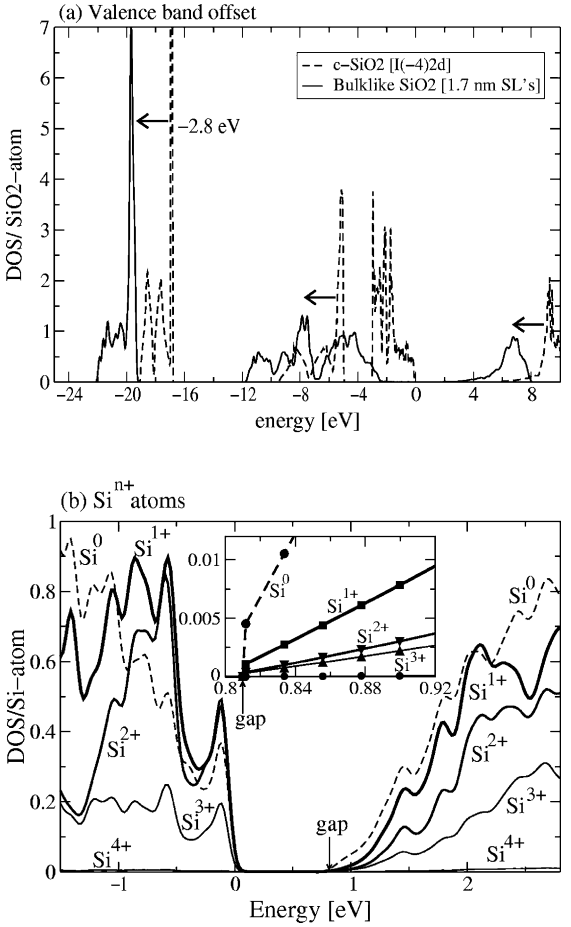

Fig. 1. (a) Evaluation of the VBO. The broken line is the DOS of bulk SiO_2; the full line is the DOS of Si^{4+} in the SL. The Fermi level is set according to the Si^0 atoms in the well. (b) Total DOS of all Si^{n+} atoms, where $n = 0, 1+, \ldots, 4+$. The inset show the DOS at the onset of the conduction band for all suboxide Si atoms.

Interface effects have been further analysed by evaluating the mean value of the densities of states (DOSs) of all suboxide Si atoms, and comparing them to their bulklike counterparts. Fig. 1(b) shows the DOS per Si atom for all Si^{n+} atoms in the 1.7 nm thick Si quantum well. We observe (see the inset of Fig. 1(b)) that all suboxide Si atoms contribute to the DOSs at the threshold of the energy gap (gap edges) of the SLs (0.81 eV within the LDA), as it is for bulklike Si atoms; they can thus be considered part of the Si well.

This is in contrast to an expected stepwise increase of the energy gaps, from the lowest value for Si^0 atoms, to intermediate values for each of the three suboxide Si atoms, and the highest value for Si^{4+} atoms. This is confirmed from previous calculations [3], where the role of the suboxides on the energy gap, as well as the electronic properties near the Fermi level, were estimated. The present calculations, further, provide a measure of the relative magnitude in the DOS of each suboxide Si atoms, below and above the Fermi level. The main part of Fig. 1(b) shows that the DOS of bulklike Si atoms (Si^0) and of Si^{1+} are nearly identical, while the DOSs of the Si^{2+} and Si^{3+} atoms are slightly damped in the conduction bands. Below the Fermi level, the DOS of bulklike Si^0 as well as suboxide Si^{1+} and Si^{2+} are comparable; the contribution of Si^{3+} is lower, but still effective. Finally, Si^{4+} atoms (which belong to the SiO_2 layer) do not contribute to the DOS.

3. Conclusions

Using structurally-relaxed Si/SiO_2 SL models containing the three types of suboxide Si atoms at their interfaces, we have obtained (within the LDA) values for the VBO and CBO, equal to 2.8 and 2.5 eV, respectively. We infer from this calculation that the experimental CBO should be lower than the VBO, by at least 0.3 eV. We have also shown that all suboxide Si atoms contribute to the DOSs at the threshold of the gap, i.e. suboxides should be considered part of the Si well.

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