Optimal interface doping at $La_{2/3}Sr_{1/3}MnO_3/SrTiO_3(001)$ heterojunctions for spintronic applications

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We examine, by means of ab initio pseudopotential calculations, $La_{2/3}Sr_{1/3}MnO_3/SrTiO_3$ (LSMO/STO) heterojunctions in which one unit layer of $La_{1-x}Sr_xMnO_3$ (with $0 < x < 1$) is inserted at the interface. The optimal interlayer doping $x$ for a robust interface ferromagnetism is investigated by considering the energy differences between antiferromagnetic and ferromagnetic alignment of the MnO$_2$-interface layer relative to bulk LSMO. The optimal doping is found to be close to $x = 1/3$, which corresponds to an abrupt TiO$_2$ (001)-layer termination of STO. This is also the composition which gives the largest $p$-type Schottky barrier height in our calculations.

Very promising magnetic tunneling junctions (MTJ’s) based on $La_{2/3}Sr_{1/3}MnO_3$ (LSMO) and SrTiO$_3$ (STO) LSMO/STO/LSMO(001)1,2 have not yet realized their full potential. Due to its large spin polarization (half or close to half metallicity) and high Curie temperature ($T_C = 370$ K), LSMO is well suited for spintronic applications, such as tunnel magnetoresistance (TMR) devices and field-effect transistors 3–5. At the same time, STO is a wide-gap semiconductor closely lattice matched to LSMO (less than 1% mismatch) and is therefore also well suited as tunneling barrier in LSMO/STO/LSMO MTJ’s. In fact, a TMR ratio as large as $\sim 1900\%$ has been measured in LSMO/STO/LSMO MTJ’s at 4 K 6.

However, the TMR ratio at higher temperatures drops significantly and vanishes well below room temperature 7–8. Origins of this behavior might lie in the presence of extrinsic defects, loss of stoichiometry, interface roughness, atomic intermixing at the interface 9,10 and canting of interface spins 11–13. Possibly, such problems could be countered by atomic-scale control of the interface properties in epitaxial growth of the heterostructures. In a pioneering study, Yamada et al. 14,15 successfully enhanced the ferromagnetism and TMR (from 50% to 170% at 10 K) of their LSMO/STO/LSMO structures; this was achieved by engineering, at the atomic scale, the interface doping profile with the growth of one bilayer of LaMnO$_3$ at the nominally SrO-terminated LSMO/STO(001) interface. However, it should be noted that their TMR values, based on the engineered SrO-terminated LSMO/STO(001) interface, were significantly lower than other reported results on unmodified LSMO/STO/LSMO(001) structures 6,15–17. More recently, Kourkoutis et al. 18 also showed that enhanced ability to control the microscopic growth and interface sharpness in LSMO/STO(001) superlattices leads to a large improvement—with the stabilization at room temperature of ferromagnetism and metallicity for LSMO thicknesses down to 2 nm 19.

Nonetheless, despite impressive progress achieved so far in the epitaxial control of the LSMO/STO interface and atomic-layer engineering of the same, some uncertainties remain in general on the details of the atomic structure. This concerns, in particular, the precise chemical stoichiometry of the interface layers, given the significant atomic intermixing typically present at such interfaces 16–18. This, in fact, hinders a precise systematic assessment of the optimal interface atomic configuration for a robust ferromagnetism—and possibly enhanced TMR—directly from experiment. Thus, a theoretical study of optimal doping remains the most direct answer to this question.

Theoretically, the two distinct chemically abrupt SrO- and TiO$_2$-layer terminations of the STO(001) at the interface are commonly assumed 15,20. A strengthening of the ferromagnetism at the LSMO/STO interface with the SrO-layer termination upon doping with one or two LaMnO$_3$ unit layers inserted at the interface was obtained performing self-interaction-corrected local spin density calculations 18. No ab initio calculation, however, has been carried out yet on the influence of layer doping on the ferromagnetism of the TiO$_2$-terminated interface. Only a model inferred from previous calculations 18,19, based on nominal charges for the Sr, La, Ti, and O ions, may be used to predict the optimal doping in this case 21. Within this model, each La$_{1-x}$Sr$_x$O layer distributes $(1-x)$ electrons over the adjacent MnO$_2$ layer(s) 18,19. For the TiO$_2$-layer termination, the model would predict an optimal doping of $x \approx 2/3$ for a La$_{1-x}$Sr$_x$MnO$_3$ unit layer inserted at the LSMO/STO interface. In this context, ab initio calculations as a function of $x$, in the full range $0 < x < 1$, are needed to provide a more precise and reliable determination of the optimal doping. A recent first-principles study 21 of the band alignment at this interface, with $x$ in the range $0.5 < x < 1$, demonstrated a strong dependence on $x$, indicating a possibility of controlling the Schottky barrier height (SBH) by changing the composition of the interfacial La$_{1-x}$Sr$_x$MnO$_3$ layer. The SBH is the fundamental interface parameter that controls the transport properties of the fully developed metal/semiconductor junction. It can also be related to the tunneling barrier in MTJ 22, although it is only an estimate in this case. The trends with $x$, however, are expected to be the same in the two
In this work, we apply the first-principles density-functional theory (DFT) to systematically explore effects of the interface layer doping, in the whole doping range, on the robustness of the ferromagnetism at the LSMO/STO(001) heterojunction. Our findings indicate an optimal doping close to \( x = 1/3 \). In addition, we calculate the \( p \)-type SBH for all the dopings considered and find that it also has the maximum value for \( x \approx 1/3 \).

Our DFT calculations were performed using the PWSCF code [23] with ultrasoft pseudopotentials [24, 25] and plane wave basis set. For exchange and correlation, we used the Perdew-Burke-Ernzerhof parametrization [26]. In our study, the \( \text{La}_{2/3}\text{Sr}_{1/3}\text{O} \) layer at the interface is replaced by \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \). Different layers in STO and LSMO are color-coded, with the interface (denoted with a black line) located between \( \text{La}_{1-x}\text{Sr}_x\text{O} \) and \( \text{TiO}_2 \) layers (\( \text{TiO}_2 \) termination of STO).

FIG. 1. A schematic representation of the interface layer doping considered in this work. The \( \text{La}_{2/3}\text{Sr}_{1/3}\text{O} \) layer at the interface is replaced by \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \). Different layers in STO and LSMO are color-coded, with the interface (denoted with a black line) located between \( \text{La}_{1-x}\text{Sr}_x\text{O} \) and \( \text{TiO}_2 \) layers (\( \text{TiO}_2 \) termination of STO).

FIG. 2. Supercells (periodically repeated) used to model the LSMO/STO(001) heterojunctions with different interface doping configurations. The regions of the supercell labeled I to V include each two monolayers forming an LSMO unit (regions I to III) or an STO unit (regions IV and V). The doping of the interface \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) layer, (in region III) takes on the values: \( x = 0 \) (a), 1/3 (b), 2/3 (c) and 1 (d). Large black, large grey, small black and small grey spheres denote \( \text{La}, \text{Sr}, \text{Mn}, \text{and Ti atoms, respectively. The grey dots indicate the O atoms.} \)
the bandgap value. We have thus used in the present work also the GGA+U which corrects the STO gap [19]. The values we use for the Hubbard U’s acting on the Ti and Mn 3d states, $U_{\text{Ti}} = 8$ eV and $U_{\text{Mn}} = 2$ eV [19], reproduce the experimental STO bandgap and LSMO half metallicity.

As a measure of robustness of the interface ferromagnetism, we have evaluated the exchange energy $E_{\text{AFM}} = E_{\text{FM}}$, i.e. the energy difference between antiferromagnetic and ferromagnetic alignment of the single MnO$_2$-interface layer relative to bulk LSMO (we always assume a ferromagnetic spin order within each MnO$_2$ plane). The calculated exchange energies are shown in Fig. 3. The results are reported for different interface doping configurations. Both GGA+U and GGA results are included for comparison. We first analyze the curves obtained for the structures in which atomic positions at the interface were optimized (“relaxed”). Our calculations reveal that the FM alignment of Mn moments is lower in energy than the AFM alignment for all considered situations with different doping levels $x$. The solid and dashed lines are cubic spline interpolations of the data sets. The energies are given in electron volt per LSMO/STO (1 $\times$ 3) interface unit. The curves denoted as “unrelaxed” are obtained for the ideal cubic perovskite atomic structure, without optimization of the atomic positions at the interface.

FIG. 3. Exchange energy for LSMO/STO(001) heterojunctions with different doping levels $x$. The solid and dashed lines are cubic spline interpolations of the data sets. The energies are given in electron volt per LSMO/STO (1 $\times$ 3) interface unit. The curves denoted as “unrelaxed” are obtained for the ideal cubic perovskite atomic structure, without optimization of the atomic positions at the interface.

In Fig. 4 we present the calculated values for the $p$-type Schottky barrier height as a function of doping, shown for the relaxed and unrelaxed cases in GGA+U and GGA. Also the values of the calculated STO band gaps (dotted lines) are shown. $E_{\text{g}}^{\text{GGA+U}}$ and $E_{\text{g}}^{\text{GGA}}$ stand for the STO bandgap values calculated in GGA+U and GGA, respectively.

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ture (“unrelaxed”), without optimization of the atomic positions at the interface. The differences between the $x$-values for optimal doping obtained for the two structures are not larger than the uncertainties of the numerical and interpolation procedures, which indicates that the result is not sensitive to the change from the ideal cubic perovskite to the optimized interface structure [33]. We also note that the $ab$ initio optimal doping is different from the predictions of the model with the nominal charges for the La, Sr, Ti, and O ions, in which the estimated optimal doping is around $x = 2/3$.

In Fig. 4 we present the calculated values for the $p$-type SBH [19] as a function of doping for GGA+U and GGA. The largest SBH within the GGA+U calculations is found at $x \approx 1/3$, i.e. at about the same composition which gives the optimal doping for ferromagnetism. It is evident that the optimization of the atomic structure does not alter the trend. For the change of $x$ from 1 to 1/3 [from SrO to TiO$_2$-terminated LSMO/STO(001)], we observe a quasi linear increase of the $p$-type SBH, in agreement with the experimental results [34] and previous theoretical findings (available for the interval $0.5 < x < 1$) [20]. This trend can be expected from the consideration of the interface dipole, which linearly increases from $x = 1$ towards lower $x$, as the electronic charge donated by the La$_{1-x}$Sr$_x$ to the Mn grows linearly. The change of trend occurs abruptly near $x = 1/3$, when the GGA+U SBH starts decreasing towards the lower value at $x = 0$. By evaluating the 3d electronic charge on the Ti and Mn ions, we established that this change of trend is due to a change in the d-valence charge of the Ti ions, from $q_d \approx 0$ ($d^0$) for $x \gtrsim 1/3$ to $q_d \approx 0.5$ e for $x = 0$ with a related decrease (by 0.1 e) of the Mn d electronic charge from $x = 1/3$ to $x = 0$. Hence, when decreasing
x from $1/3$, an increasing amount of the $La_{1-x}Sr_x$ electronic dopant charge is transferred to the neighboring Ti ions rather than to the Mn ion. This charge transfer causes a dipole moment of opposite orientation, which partially cancels the original $La_{1-x}Sr_x - Mn$ dipole and thus lowers the SBH. In fact, a similar charging of the interfacial Ti was previously reported experimentally at the STO/$LaMnO_3(001)$ interface [35]. We note that the deviation from the nominal valence charge for the Ti ions for $x < 1/3$ also implies that the model description considering the Mn as the only mixed valence ions loses its validity for $x \lesssim 1/3$. This, together with the model-inherent constraints and approximations in the description of the valence charge for all $x$, clearly limits its predictive capabilities for a quantitative assessment of the optimal doping.

In this paper, we have calculated the optimal doping for a robust ferromagnetism at the LSMO/STO interface by means of first-principles DFT calculations and obtained the value $x \approx 1/3$. It corresponds to the concentration for which the interface becomes abrupt with the $TiO_2$ termination of STO. At about the same composition, we find that the $p$-type SBH has the maximum value.

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