Strain effects on the electronic properties in δ-doped oxide superlattices

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An error was made in the typesetting of figures 2, 3 and 5 of the published article. The embedded text values in the figures were omitted. The figures should look as follows:

![Figure 2](image-url)
Additionally the Acknowledgment should read: The research at SMU was supported by the Semiconductor Research Corporation (J H Y). Research at ORNL was sponsored by the U S Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Divison (J H L, S O, V R C, H N L) and the Office of Science Early Career Research Program (V R C).
1. Introduction

Strain engineering has been successfully utilized in metal-oxide-semiconductor field-effect transistors (MOSFET) to improve device performance. Modulating strains in MOSFET channels tailors important electronic material properties, such as band-edge energies, effective masses, scattering centers, etc to enhance the transport of 2D electron gases (2DEGs) in the channels [1, 2]. Recently, metallic behavior has been observed in transition-metal oxide heterostructures where carriers are strongly localized near the interfaces to form 2DEGs [3, 4]. Among possible combinations of transition-metal oxide heterostructures, SrTiO$_3$-based heterostructures containing strongly correlated electron oxides (e.g. LaAlO$_3$/SrTiO$_3$ (LAO/STO) [5, 6], LaTiO$_3$/SrTiO$_3$ (LTO/STO) [7, 8]) are of great interest because of the coexistence of strong correlation and quantum confinement [3, 4, 9–11]. These heterostructures have shown a great potential for developing future applications based on intriguing properties including high carrier mobility [12–14], superconductivity [15, 16], electric-field controlled resistance [17], novel magnetism [18–20] and large thermoelectric power [21–24].

Unlike LAO/STO heterostructures where the carriers originate from either charge transfer [10] or oxygen vacancies [25], the conducting carriers in La$_{\delta}$-doped STO heterostructures are from the electronic reconstruction between the occupied Ti 3$d^1$ state in LTO and the empty Ti 3$d^0$ state in STO. The Ti 3$d$ state at the interfaces becomes 3$d^{0.5}$ and as a result, the metallic LTO/STO interface has the carrier density of ~0.5 e/u.c. per interface [13, 26, 27]. The conducting Ti 3$d$ electrons spread over a few unit cells (u.c.) with the change in orbital-ordering among Ti 3$d$ t$_{2g}$ electrons; the $d_{xy}$ orbital electrons are highly localized at the interfaces, while the degenerate $d_{xz}$ and $d_{yz}$ states extend into the STO spacer region [28, 31].
Previous investigations on the effects of fractional doping concentrations and STO spacer thicknesses have revealed a way to design the electron transport characteristics in LTO/STO superlattices. Ong et al. [32] employed density functional theory (DFT) and demonstrated the dimensionality crossover between 3 and 2D electronic behavior in Sr$_{1-x}$La$_x$TiO$_3$/SrTiO$_3$ (SLTO/STO) superlattices. Choi et al. [8] also investigated the effects of fractional doping concentrations on insulator–metal transitions in SLTO/STO superlattices. You and Lee [31] studied the effects of STO spacer thicknesses in (LTO)$_n$(STO)$_m$ superlattices and found that a 2DEG is formed from $d_{xy}$ orbital electrons when $N \geq 3$. More recently, we demonstrated that these $d$-doped superlattices remain transparent even as the transport changes from 2 to 3D conductivity [33]. However, the effect of strain has not been studied in depth.

In this work, we demonstrate that strain can serve as an efficient tool for tuning the electronic properties in oxide heterostructures. Taking LTO/STO superlattices as a prototypical system, we show that biaxial in-plane (xy plane) strain enhances or suppresses the splitting between $d_{ox}$ and $d_{zc}$ ($d_{zc}$) orbitals, resulting in a drastic change in the transport dimensionality between 2 and 3D.

2. Calculation details

To investigate the effects of biaxial in-plane strains in (LTO)$_n$(STO)$_m$ superlattices with $1 \leq N \leq 6$, we performed DFT calculations using the Vienna ab initio simulation package (VASP) [34, 35]. All DFT calculations were carried out with the projector augmented wave (PAW) approach [36], an energy cutoff of 500 eV and the rotationally invariant LSDA + U method [37]. We used $U = 5$ eV and $J = 0.64$ eV for Ti $d$ states [30, 38] and $U = 11$ eV and $J = 0.68$ eV for La $f$ states [30]. With the LSDA + U method, the lattice constant of cubic STO was calculated as 3.892 Å. To modulate the biaxial in-plane strain, the lattice constants of the $xy$ plane were fixed as $a_{xy} = a_{xy} = 3.697$, 3.775, 3.910 Å (experimental STO cubic lattice [3]), 4.009 and 4.087 Å which correspond to biaxial in-plane strains of $\varepsilon_{//} = 5\%$ and $\varepsilon_{//} = 0\%$, $\varepsilon_{//} = -3\%$, $\varepsilon_{//} = 0\%$, $\varepsilon_{//} = 5\%$, and $\varepsilon_{//} = 5\%$, respectively. The out-of-plane ($z$ axis) lattice vector was optimized within the tetragonal $P4mm$ space group and all ionic positions were relaxed until all Hellmann–Feynman forces were smaller than 5 meV Å$^{-1}$. The lattice vector and ionic positions were optimized using a $6 \times 6 \times n k$-point grid where $n = 6/(N + 1)$. Subsequent band structures were determined with a finer $k$-point mesh of $24 \times 24 \times n$ where $n = 24/(N + 1)$. Additional calculations were performed in which inversion symmetry was broken by displacing the Ti atoms along the $z$ direction under $\varepsilon_{//} = -5\%$ and along the $xy$ direction under $\varepsilon_{//} = 5\%$. In all cases, the structures relaxed to the structures determined without these distortions.

3. Results and discussion

We start our discussion from the spatial distributions of Ti 3$d$ electrons in our prototypical (LTO)$_1$(STO)$_4$ superlattices with various in-plane lattice constants. The Ti 3$d$ electron charges were obtained by integrating the occupied states in the Ti 3$d$ densities of state (DOS). The total electron density was $\sim 0.7$ e/u.c. for a Ti Wigner radius of 1.217 Å. It is important to note that the total DOS below the Fermi level indeed summed up to 1 e/u.c. (i.e. 0.5 e/u.c. per interface) and the $d$-electron density is simply an artifact of the Ti Wigner radius. As such, the $d$ electron density has been normalized to be 1.0 e/u.c. The resulting layer-by-layer electron density is plotted in figure 1. Our previous work, using the experimental STO cubic lattice of $a_0 = 3.910$ Å (i.e. $\varepsilon_{//} = 0.5\%$), found that the $d_{xy}$ orbital electrons are highly localized near the interfaces and the $d_{zc}$ and $d_{xc}$ orbital electrons are more distributed in STO [31]. For the range of strain considered here, $-5\% \leq \varepsilon_{//} \leq 5\%$, this spatial distribution pattern of $t_{2g}$ $d$-orbital electrons remains qualitatively unchanged as shown in figure 1. However, the relative occupation between Ti $t_{2g}$ orbitals is found to be strongly dependent on the in-plane strain. More specifically, we observe that as the in-plane strain increases from $\varepsilon_{//} = -5\%$ to $\varepsilon_{//} = 5\%$, $n_{xy}$ increases while $n_{xc}$ decreases. This change is reflected in the changes in the spatial distribution of the total electron density. As shown in the inset of figure 1, Ti 3$d$ electrons accumulate at the interfaces under tensile strain due to the increase in $d_{xy}$ occupation, while Ti 3$d$ electrons spread inside STO under compressive strains with the predominant $d_{xc}$ and $d_{zc}$ occupations.

Now we turn to the dynamical properties of our strained superlattices. Figure 2 shows the DOS projected onto each Ti $t_{2g}$ orbital. While the integration of the DOS below the Fermi level essentially gives the same information as the charge density distributions, the detailed structure in DOS provides information about carrier dynamics. At each Ti site, the DOS with spin-up (spin-down) states are shown in the upper (lower) panel. In (LTO)$_1$(STO)$_1$ structure under a tensile strain of...
$\epsilon_{//} = 5\%$, the $d_{xy}$ orbital is lower in energy than the $d_{yz}$ ($d_{xz}$) orbital by $0.4$ eV. As the in-plane strain decreases, the energy of the $d_{xy}$ orbital increases while that of the $d_{yz}$ and $d_{xz}$ orbitals decrease. With a compressive strain of $\epsilon_{//} = -5\%$, the $d_{yz}$ and $d_{xz}$ orbitals become even lower than the $d_{xy}$ orbital in the (LTO)$_1$/STO) structure. As the thickness of the STO spacer increases, the energy of the $d_{xy}$ orbital decreases until $N = 3$ u.c. [31]. At $N = 3$ u.c. staircase-like increments (marked as 0 and 1 in figure 2) appear in the $d_{xy}$ DOS at Ti$_{b,5}$ sites. These staircase-like increments in DOS are due to the formation of 2DEG by the $d_{xy}$ orbital electrons at the interfaces and their quantized energy levels remain quantitatively similar for $N \geq 3$ u.c. because of the fully developed LaO-induced potential wells [31, 39]. Within the range of $\pm 5\%$ in-plane strain, the minimum STO thickness to have the $d_{xy}$-orbital 2DEG is the same as 3 u.c. However, the quantized energy levels of the $d_{xy}$-orbital 2DEG change drastically with the application of in-plane strain. The lowest quantized energy level of the 2DEG (marked as 0) under $\epsilon_{//} = 5\%$ is $-0.5$ eV lower than that under $\epsilon_{//} = -5\%$. The decreased quantized energy levels of the 2DEG under tensile in-plane strain induce more 2D carriers in the system.

We further investigate the low-energy electronic properties, i.e. transport and its anisotropy governed by the band structures near Fermi-level. Figure 3 shows the conduction band structures for spin-up states along $Z$-$\Gamma$-$X$. In the (LTO)$_1$/STO) structures, the energies of the $d_{xy}$ bands decrease as the in-plane strain changes from compressive to tensile whereas those of the $d_{yz}$ and $d_{xz}$ bands increase. From the $\Gamma$ point in the (LTO)$_1$/STO) band structures, the effective masses of $d_{xy}$ are obtained as $m_{//} = 0.4 m_0$ (i.e. along the interfaces) and $m_{zz} = 2.7$–$3.7 m_0$ (i.e. perpendicular to the interfaces) for $-5\% \leq \epsilon_{//} \leq 5\%$. The $d_{yz}$ ($d_{xz}$) orbital has the effective masses of $m_{xx} (m_{yy}) = 2.8$–$4.1 m_0$, $m_{yy} (m_{xx}) = 0.47$–$0.55 m_0$ and $m_{zz} = 0.41$–$0.53 m_0$. These finite effective masses indicate that all $d_{xy}$, $d_{yz}$ and $d_{xz}$ orbital electrons can travel both along...
and perpendicularly to the interfaces in the (LTO)_{1/STO}N structures.

As the thickness of the STO spacers increases, the energies of the \(d_{xy}\) orbital bands decrease until \(N = 3\) u.c. [31]. When \(N = 3\) u.c. the \(d_{xy}\) orbital bands become flat along \(\Gamma-Z\) (marked as 0 and 1 in figure 3), creating the staircase-like increments in the Ti\(_{0.5}\)\(d_{xy}\) DOS as shown in figure 2. Since the band effective mass is inversely proportional to the band curvature, the electrons in the \(d_{xy}\) flat bands are too heavy for transport perpendicular to the interface. However, they can still transport along the interfaces with the finite effective mass of \(m_{//} = ~0.4 m_0\). Therefore, the electrons in the \(d_{xy}\) flat bands are 2DEG which can travel only along the interfaces and their \(k_z\)-independent energies are the quantum confined energies in the potential wells. As the in-plane strain changes from compressive to tensile, the energy levels of the \(d_{xy}\) flat bands decrease so that more \(d_{xy}\) 2D states become populated. In contrast to the \(d_{xy}\) bands, the \(d_{xz}\) and \(d_{yz}\) orbital bands increase in energy as the strain changes from compressive to tensile and their finite effective masses indicates the 3D transport characteristics of \(d_{xz}\) and \(d_{yz}\) orbitals.

Figure 4(a) shows the strain effects on the electron densities of \(d_{xy}\) and \(d_{xz}\) (\(d_{yz}\)) orbitals as a function of STO spacer thickness. The tensile in-plane strain and thick STO spacers increase the \(d_{xy}\) charge density, but decrease the \(d_{xz}\) and \(d_{yz}\) densities. Since the \(d_{xy}\) electrons contribute to the 2DEG when \(N \geq 3\) u.c. whereas the \(d_{xz}\) and \(d_{yz}\) electrons are always 3D, the ratios of 2D to 3D carriers available in (LTO)_{1/STO}N superlattices can be obtained as \(n_{2\text{DEG}}/\left(n_{xz} + n_{yz}\right)\). As shown in figure 4(b), the tensile strain generates more 2D carriers whereas the compressive strain induces more 3D carriers available in the superlattices. These results illustrate that the in-plane strain can be used as a control parameter to tune the transport dimensionality between 2D and 3D in the (LTO)_{1/STO}N superlattices.

A remaining question is why the \(t_{2g}\) level splitting is as large as 0.8 eV in superlattices with thick STO spacers. Here, we discuss its origin based on a microscopic model. Among various contributions, we consider (1) the actual splitting in the Ti \(t_{2g}\) level (Jahn–Teller type effect mainly from the Coulomb force originating from the surrounding \(O^{2-}\) ions), (2) the confinement potential and (3) the modulation in Ti \(t_{2g}-O\) p hybridization. To separate these three contributions, we first performed the DFT calculations for strained bulk STO. As shown in figure 5, applying \(\pm 5\%\) biaxial strains to STO induces a splitting between the \(d_{xy}\) and \(d_{yz}(d_{xz})\) bands of about 0.2 eV at the \(\Gamma\) point. In a \(d-p\) model as adopted in [40], Ti-O hybridization alone does not induce the splitting in the Ti \(t_{2g}\) level because Ti \(t_{2g}\) and O \(p\) are decoupled at the \(\Gamma\) point. Thus, the splitting shown in the bulk

![Figure 3. Bandstructures of (LTO)_{1/STO}N superlattices with \(N = 1, 3\) u.c. for spin-up states within the first Brillouin zone. Only conduction bands are shown here. The Fermi level is at 0 eV. Blue solid lines represent the \(d_{xy}\) orbital bands and red dotted lines are for the \(d_{xz}\) and \(d_{yz}\) bands.](image)
DFT calculations mainly comes from the contribution (1). This splitting is comparable with those in (LTO)$_1$/ (STO)$_1$ superlattices where the splitting is 0.40 and 0.25 eV under 5 and −5% strains, respectively (see figure 3). Therefore, for the superlattices with thin STO spacers, this appears to be the dominant contribution. On the other hand, the splitting increases significantly to 0.77 and 0.87 eV in the (LTO)$_1$/ (STO)$_3$ and (LTO)$_1$/ (STO)$_5$ superlattices, respectively, with $\varepsilon_{y} = 5\%$. Such a large splitting is hard to ascribe to the contribution (1). To see the effects of the other contributions (2) and (3), we then consider the strong confinement limit where only two Ti layers exist neighboring to a La layer coupled with five surrounding oxygen ions per unit cell via $\pi$ hybridization $t_{pd}$ by extending the $d$–$p$ model in [40]. The lowest energy level for $d_{yz}$ and $d_{xz}$ bands is found to be $\left(\Delta + \sqrt{\Delta^2 + 4t_{pd}^2}\right)/2$ with $\Delta$ being the Ti $t_{2g}$ level measured from O $p$, while the lowest level for $d_{xy}$ is just $\Delta$. Therefore, the splitting between $d_{xy}$ and $d_{yz}(d_{xz})$ could become as large as $\sim t_{pd}^2/\Delta$, i.e. the effective nearest-neighbor Ti–Ti hopping. With the additional contribution coming from Coulomb repulsive force due to $O^{2-}$ ions (1), this mechanism well explains the large $t_{2g}$ splitting observed in the superlattices with $N \geq 3$ u.c. In our DFT calculations for superlattices, we also asymmetry between $\varepsilon_{y} > 0$ and $\varepsilon_{y} < 0$. Under tensile strain at $\varepsilon_{y} > 0$ (compressive strain at $\varepsilon_{y} < 0$), the distance between Ti and apical oxygen decreases (increases). With the additional contribution (1), this results in a larger (smaller) $t_{pd}$ and a larger (smaller) splitting between $d_{xy}$ and $d_{yz}(d_{xz})$. This behavior is also consistent with our DFT results.

4. Conclusion

The strain effects on the electron transport properties in the (LTO)$_1$/ (STO)$_N$ superlattices have been investigated using DFT calculations. For $-5\% \leq \varepsilon_{y} \leq 5\%$, the $d_{xy}$ electrons are highly localized at the interfaces whereas the $d_{yz}$ and $d_{xz}$ electrons are more distributed in the STO spacers. With $N \geq 3$ u.c. the $d_{xy}$ electrons become 2DEGs which can transport along the interfaces with $m_{//} = 0.4m_{0}$, but cannot move perpendicularly to the interfaces. The quantized energy levels of the 2DEG are strongly dependent on the in-plane strain. As the in-plane strain changes from compressive to tensile, the
quantized energy levels of the $d_{xy}$ 2DEG decrease so that more 2DEG become available in the system. In contrast to the $d_{xy}$ orbital, the $d_{xz}$ and $d_{yz}$ orbitals always have 3D transport characteristics and their energy levels increase as the strain changes to tensile. Since the charge densities in the $d_{xy}$ orbital and the $d_{xz}$ and $d_{yz}$ orbitals respond to biaxial in-plane strain in an opposite way and only $d_{xy}$ electrons contribute to 2D conductivity, the transport dimensionality of the majority of the carriers can be controlled between 2D and 3D by applying a biaxial in-plane strain. Applying tensile in-plane strain generates more 2D carriers whereas compressive in-plane strains induce more 3D carriers in the superlattices. Therefore, in addition to the fractional $\delta$-doping and STO spacer thicknesses, in-plane strain can be a viable option for tuning the transport dimensionality in the La $\delta$-doped STO superlattices.

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