An all-perovskite $p$-$n$ junction based on transparent conducting $p$-La$_{1-x}$Sr$_x$CrO$_3$ epitaxial layers

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Transparent, conducting $p$-La$_{1-x}$Sr$_x$CrO$_3$ epitaxial layers were deposited on Nb-doped SrTiO$_3$(001) by oxygen-assisted molecular beam epitaxy to form structurally coherent $p$-$n$ junctions. X-ray photoelectron spectroscopy reveals a type II or “staggered” band alignment, with valence and conduction band offsets of 2.0 eV and 0.9 eV, respectively. Diodes fabricated from these heterojunctions exhibit rectifying behavior, and the $I$-$V$ characteristics are different from those for traditional semiconductor $p$-$n$ junctions. A rather large ideality factor is ascribed to the complex nature of the interface.

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Translucent conducting oxides (TCOs) are of significant interest in optoelectronics.1–3 Most of the known TCOs are $n$-type (e.g., In$_2$O$_3$, ZnO, and SnO$_2$).3 There is thus a critical shortage of $p$-type TCOs, limiting the use of these materials in solar cells, light emitting diodes, and all-transparent junctional devices.4,5 The most widely studied $p$-TCOs to date are based on SnO, spinel structured oxides (ZnM$_2$O$_4$, $M$ = Rh, Co, etc.), layered oxylchalcogenides, and delafossites, such as AgM$_2$O$_3$ and CuM$_2$O$_3$ (M = trivalent cation, such as Al, Ga, and In).6–8 Due to structural incompatibilities between $n$- and $p$-type TCOs and metastable valences, oxide $p$-$n$ junctions exhibit poorly ordered interfaces, leading to problems in the fabrication of reliable devices.9

High-quality perovskite oxide (ABO$_3$) thin film $p$-$n$ junctions have significant potential for electronic devices with multifunctional properties.6–13 However, the $p$-type perovskites currently in use are not sufficiently transparent in the visible region. We have previously demonstrated that alloying Sr and La at the A-sites of perovskite LaCrO$_3$ (LCO) can effectively introduce holes at the top of the valence band, resulting in $p$-type conductivity while maintaining reasonable transparency to a Sr mole fraction ($x$) of $\sim 0.25$.14 Therefore, epitaxial growth of La$_{1-x}$Sr$_x$CrO$_3$ (LSCO) ($x = 0.25$) on Nb-doped perovskite SrTiO$_3$ (Nb:STO) can in principle yield an all-perovskite $p$-$n$ heterojunction with a structurally coherent interface ($\Delta a/a = -0.68\%$ to $-0.88\%$ for $x = 0.1$ to 0.2).

La$_{1-x}$Sr$_x$CrO$_3$ ($0.12 < x < 0.15$) films ranging from 2 nm [$\approx 5$ unit cells (u.c.), 1 u.c. $\approx 3.88 Å$] to 30 nm were grown on Nb:STO(001) (0.05 wt. % Nb, Crystec GmbH) by oxygen assisted molecular beam epitaxy (OAMBE). The films grew in a layer-by-layer fashion as revealed by reflection high-energy electron diffraction (RHEED) intensity oscillations and ex situ atomic force microscopy (AFM) studies, as seen in Fig. S1 in the supplementary material. The electronic structure, band offsets, elemental composition, interface structure, and transport properties of the LSCO films were characterized by high-resolution x-ray photoelectron spectroscopy (XPS), scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (STEM-EELS), and electrical transport measurements. Additional details are provided in the supplementary material.

We first examine the composition and structure of LSCO/Nb:STO(001). Typically, $p$-$n$ heterojunction models are based on an atomically abrupt interface, although it is widely recognized that there is some extent of cation mixing at substrate temperatures high enough to enable epitaxial growth.15–19 Cation exchange across the interface generates anti-site defects that can act as donors or traps for electrons or holes, thus affecting transport characteristics. Figure 1 shows the Sr 3d and Ti 2p core-level spectra for a 5 u.c. LSCO film on Nb:STO. This film thickness was chosen to be large enough so that the electronic structure of the LSCO is likely to be fully developed, yet thin enough to yield a sufficient photoemission signal from the substrate such that heterojunction electronic properties can be extracted from the spectra. The Sr 3d spectrum [Fig. 1(a)] can be fit using two sets of spin-orbit (SO) doublets. The more intense, higher binding energy pair (red, at 133.3 and 135.1 eV) is assigned to Sr$^{3+}$ in Nb:STO. This assignment is based on the large intensity of these features and their binding energies in light of the value of $E_{Sr3d5/2} - E_V$ [130.55(4) eV] for pure Nb:STO, as discussed in more detail below. The weaker, lower binding energy pair (blue) is assigned to Sr atoms that occupy A-sites in the LSCO film. The binding energy difference ($\sim 0.9$ eV) is due to the valence band offset.
and differences in the overall electrostatic environments in II-IV and III-III cubic perovskites. The Ti 2p$_{3/2}$ spectrum [Fig. 1(b)] can also be fit using two Voigt functions separated by $\sim$0.9 eV. The higher binding energy peak (red) at 458.65 eV is assigned to Ti$^{4+}$ in the Nb:STO substrate, again based on the value of $E_{Ti2p_{3/2}} - E_V$ [455.95(4) eV] for pure Nb:STO.\textsuperscript{20} The weaker, lower binding energy peak (blue) is assigned to Ti cations in the LSCO film. We rule out the possibility that this peak is due to Ti$^{3+}$ in the Nb:STO resulting from La in-diffusion and doping because the binding energy difference between Ti$^{3+}$ and Ti$^{4+}$ in La-doped STO is larger, $\sim$1.5 eV.\textsuperscript{21} The average formal charge for all B-site cations in LSCO with $x = 0.12$ is $\pm 3.12$. Accordingly, if out-diffused Ti cations are randomly distributed at B-sites in the LSCO film, their average charge would also be $\pm 3.12$. However, if out-diffused Sr and Ti cations are structurally correlated (i.e., in adjacent A and B sites), the Ti would have a formal charge much closer to $\pm 4$. Given the much greater stability of Ti$^{4+}$ compared to Ti$^{3+}$, we tentatively conclude that out-diffused Ti and Sr are indeed structurally correlated, as are La and Cr co-dopants in STO films.\textsuperscript{19,22} Thus, the 0.9 eV binding energy difference between the two features in the Ti 2p$_{3/2}$ spectrum is ascribed to differences in band alignment and in the overall electrostatic potential. This difference is somewhat smaller (0.6 eV) for Ti$^{4+}$ in NdTiO$_3$ with absorbed interstitial oxygen and STO.\textsuperscript{23}

STEM-EELS measurements also reveal cation mixing. Figure 2(a) shows a representative cross-sectional high-angle annular dark field (STEM-HAADF) image for a 30 nm LSCO/Nb:STO(001) heterojunction taken along the [100] zone-axis. The interface is structurally coherent and free of misfit dislocations. A sharp change in Z-contrast at the interface is also plainly visible, and gives the impression that the interface is atomically abrupt. However, STEM-EELS maps for the Sr $L_{2,3}$, Ti $L_{2,3}$ and La $M_{4,5}$ edges, shown in Figs. 2(b)–2(e), reveal otherwise. These maps are based on raw, power law background-subtracted energy loss signals, since it was found that noise reduction via principal component analysis (PCA) introduces artifacts that distort the local concentrations.\textsuperscript{24,25} We do not show the Cr $L_{2,3}$ edge map since its overlap with the O K edge continuum precludes accurate background subtraction and signal integration. Gaussian fitting to the atomic positions yields the following full width at half maximum (FWHM) values: Sr $L_{2,3} = 0.32$ nm, Ti $L_{2,3} = 0.36$ nm, and La $M_{4,5} = 0.36$ nm (all $\pm 0.01$ nm). The diffuse background between lattice sites is the result of beam delocalization and channeling effects, which can complicate the interpretation of the absolute interface width.\textsuperscript{26} Using a logistic fit to 90%/10% extrema on either side of the interface, the apparent interface widths are: $\delta_{Sr} = 1.29 \pm 0.34$, $\delta_{Ti} = 1.49 \pm 0.07$, and $\delta_{La} = 1.65 \pm 0.15$ nm. Based on these numbers, the apparent extent of intermixing is as high as 4 u.c. (for La). A comparable extent of mixing has been
observed in \( p\)-Pr\(_{0.64}\)Ca\(_{0.36}\)MnO\(_3\)/n-STO(001) heterojunctions.\(^{13}\) Energy-dispersive X-ray spectroscopy (STEM-EDS) analysis, reported elsewhere, yields comparable results. However, we find that the accuracy of the interface measurement is sensitive to cross-sectional foil thickness and that 1–2 u.c. of uncertainty is estimated for the present sample, depending on the core edge.\(^{27}\)

Oxygen vacancies (\( V_O \)) can substantially affect and even dominate electrical transport properties in transition metal (TM) oxides.\(^{16,28–30}\) Manganites, titanates, and zirconates, exhibit different resistance states at opposite polarities of electrical stimulation.\(^{31–33}\) Such so-called bipolar resistive switching can lead to memristive devices and is widely believed to result from the diffusion of \( V_O \) under the influence of an electric field. Measuring valence changes in the transition metal (TM) cations is a useful way to detect \( V_O \) since each \( V_O \) donates two electrons to the lattice that can reduce adjacent TM cations. Returning to Fig. 1(c), we show Cr 2p spectra from MBE-grown LCO (Cr\(^{3+}\)), SrCrO\(_3\) (SCO, Cr\(^{4+}\)), and a LSCO film with \( x = 0.12 \), respectively. The Cr 2p spectrum for the LSCO film can be well reproduced by a linear combination of the LCO and SCO reference spectra with weighting factors of 0.88 and 0.12, respectively.\(^{34}\) If \( V_O \) were present at concentrations exceeding a few percent, we would need a larger (smaller) weighting coefficient for LCO (SCO). The excellent match using weighting factors corresponding to the Sr concentration indicates that the \( V_O \) concentration is below the XPS detection limit. Additionally, \( I-V \) curves measured across the LSCO/STO heterojunction do not change with the voltage sweep polarity, as shown in Fig. S2 (supplementary material), further supporting the conclusion that the \( V_O \) effect is negligible.

Band alignment was determined using XPS.\(^{35–38}\) We utilized the Sr 3d and La 4d core levels due to their proximity to the VB,\(^{39}\) along with band gap values of 2.1 eV for LSCO\(^{14}\) and 3.25 eV for STO.\(^{40}\) The resulting valence band offset (VBO) and conduction band offset (CBO) values are 2.0(1) eV and 0.9(1) eV, respectively. In order to determine band bending, we compare binding energies for the clean substrates with those for films of various thicknesses. Figures 3(a) and 3(b) show representative Ti 2p and Sr 3d spectra for the clean Nb:STO substrate and after the deposition of a 5 u.c. LSCO film. The Ti 2p\(_{3/2}\) and Sr 3d\(_{5/2}\) binding energies prior to film deposition are 459.06 eV and 133.65 eV, respectively. Thus, the valence band maximum (VBM) is 3.1 eV below the Fermi level (\( E_F \)), indicating slight (<0.15 eV) upward and bending. After growth of 5 u.c. of LSCO, both the Ti 2p\(_{3/2}\) and Sr 3d\(_{5/2}\) substrate peaks shift 0.4 eV to lower binding energy, indicating additional upward band bending with a VBM of 2.7 eV below \( E_F \). Upward band bending is observed in the LSCO by comparing the La 4d binding energy and the VBM values in the 5 u.c. and 38 u.c. films. The top of the LSCO VB from 0 to \( \sim 3 \) eV is dominated by Cr 3d\(_{2g}\) character. As a result, even though the VB spectrum for 5 u.c. LSCO/STO contains contributions from both materials, extrapolating the leading edge to the energy axis reveals the position of the VBM in the LSCO. The quantity \( E_{La4d5/2} - E_V \) is 101.2(1) eV for the 38 u.c. LSCO film. At 5 u.c., the La 4d\(_{5/2}\) binding energy is 101.9(1) eV, revealing that the LSCO VBM is 0.7(1) eV below the Fermi level. The same VBM value is derived directly from the VB spectrum (Fig. 3(d)). At 38 u.c., the VBM is 0.4(1) eV below the Fermi level. This comparison establishes the approximate magnitude and sign of the built-in potential within the LSCO films. Figure 4(a) summarizes these
results. The type II staggered band alignment and the associated built-in potentials are favorable for the separation and transport of photo-generated electrons and holes. As such, this heterojunction could be useful as part of a photoanode to facilitate the oxygen evolution reaction in photoelectrochemical water splitting, as well as in photovoltaic cells.

Electrical properties were probed by fabricating vertical transport junctions, as illustrated in the inset of Fig. 4(b). The top metallization pads (30 nm Cr and 70 nm Au) were deposited by sputtering and 50 μm in diameter. A 50 nm blanket Au film was deposited on the back side of Nb:STO. Temperature-dependent I-V measurements were performed in which forward bias is defined as positive DC voltage on the p-LSCO film surface. A set of representative I-V curves is shown in Fig. 4(b), clearly indicating rectifying behavior. From our previous studies, it is known that both the ionized hole concentration and mobility in LSCO films increase with increasing temperature.\(^{34}\) As a result, the conductivity of LSCO increases exponentially with temperature, as shown in Fig. 4(c). This result explains the observation that both forward-bias current and reverse leakage current increase with increasing temperature, as indicated by the arrows in Fig. 4(b). At room temperature, the asymmetry ratio, defined as \(\beta = I(1.5\, \text{V})/I(-1.5\, \text{V})\), is \(\sim 32\). Smaller threshold voltages \(V_D\) and higher forward currents are observed with increasing temperature, as also found in other oxide \(p-n\) junctions.\(^ {7,9,11-13}\) The slopes of the I-V curves (corresponding to junction resistance) near the threshold voltage under forward bias become steeper, as more carriers are driven across the interface at higher temperatures. We can approximate the forward bias current using\(^ {41}\)

\[
I = I_0 \exp \left( \frac{qV}{nk_BT} \right). \tag{1}
\]

Here \(I_0\) is the temperature-dependent saturation current prefactor, \(q\) is the elementary charge, \(V\) is the applied voltage, \(k_B\) is the Boltzmann constant, \(T\) is temperature, and \(n\) is the ideality factor. The ideality factor is known to depend on both the electronic structure of the \(p-n\) junction and the associated mechanism of charge transfer.\(^ {13,42}\) We find for these diodes that \(n \geq 8\) for all temperatures investigated; such a significant deviation from unity has also been observed in other oxide \(p-n\) junctions.\(^ {43-46}\) In addition, according to the energy band diagram shown in Fig. 4(a), the CBO is much smaller than the VBO. Thus, electrons should be the dominant carriers under forward bias, and an applied voltage of \(\sim 1.4\, \text{eV}\) is expected to overcome this barrier. However, the threshold voltages for our diodes are \(\leq \sim 1.0\, \text{V}\). The lower-than-expected threshold voltages and large ideality factors suggest that electrically active defects exert a measurable influence. Anti-sites resulting from cation intermixing (La\(_{Sr}\) shallow donors, Cr\(_{Ti}\) deep acceptors, and Ti\(_{Cr}\) deep donors) may act as carrier traps and/or sources and thus modify the I-V characteristics.

Finally, we note that Nb:STO substrate quality and preparation are critical for the fabrication of these \(p-n\) junctions. The quality of oxide substrates can vary greatly from different vendors and different batches. In our studies, the I-V characteristics were often found to be dominated by mesoscale defects on the substrate surfaces. When the defect concentration on the substrate surface was high, many individual diodes exhibited short circuit rather than rectifying behavior. In Fig. S3 (supplementary material), we show that step bunching and etch-induced pits at the substrate surface can cause non-crystalline film growth. I-V curves measured near such defects using conductive AFM show Ohmic behavior.

In summary, LSCO/Nb:STO heterojunctions exhibit a type-II staggered band alignment and rectifying behavior, as expected from a \(p-n\) junction. Non-idealities in the I-V curves are correlated with the presence of cation anti-sites resulting from interdiffusion over a few unit cells. The electronic properties of these heterojunctions are favorable for photo-generated electron/hole pair separation. Our work suggests that as a \(p\)-type TCO, LSCO can potentially be
integrated with other perovskites or traditional semiconductors, such as Si and Ge, for use in advanced photovoltaics, photochemical water splitting, and other multifunctional applications involving perovskites.

See supplementary materials for details on film growth and characterization.

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