Supplementary material for New Journal of Physics article entitled: “Contribution of Jahn-Teller and charge transfer excitations to the photovoltaic effect of manganite/titanite heterojunctions”

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Abstract: In this supplementary material we provide optical absorptance measurements of the manganite absorber and the STNO substrate. Here it is clearly visible that this type of model system allows investigating the photo generation of excess charge carries separately in the manganite and titanite. Structural characterizations of the interface of the heterojunction were performed in order to prove the crystalline quality of the junctions, which were analyzed by means of transmission electron microscope. In addition a comparison of the different junctions of the current-voltage characteristics in the dark is provided.

a) Optical properties of manganites and titanites

Spectrally resolved absorption of the different involved materials was investigated with a Varian Cary 50 system. Using pristine STNO substrates and about 85 - 100 nm thick PCMO and 75nm thick CMO films on double side polished MgO, the reflectance and the transmittance were measured in the photon energy range from 1 to 4 eV. The absorptance was calculated according to

\[ \alpha = 1 - \frac{I_R + I_T}{I_0}, \]

(6)
where $I_0$, $I_R$ and $I_T$ are the incident, the reflected and the transmitted power at a given photon energy. Baseline corrections were performed to eliminate signals from the empty holder and the used mirror systems. We have not considered the MgO substrate of the thin film samples, since small corrections due to the weak absorptance of MgO below the measured bandgap of 5.3 eV will only slightly change the spectrally dependent absorptance of the manganites. For MgO also values of $E_G$ up to 7.8 eV are reported [1].

The spectrally resolved absorptance of PCMO, CMO and STNO is shown in figure S1. The measurements were performed at room temperature but additional control experiments in a Cary Varian 5e spectrometer system equipped with an Oxford Fast track Microstat H$_2$ gas flow cryogenic system at different temperatures show that the height and the energy position of the optical features only marginably change with temperature, i.e. figure S1 is typical also for lower temperatures.

![Figure S1](image)

Figure S1. Spectrally resolved absorptance of PCMO, CMO and STNO at room temperature. Both manganite films exhibit a charge transfer transition between O2p and minority spin Mn 3d $t_{2g}$ and $e_g$ states. In contrast to CMO an additional NIR polaron absorption band is present in PCMO which involves Jahn-Teller split Mn $e_g$ states hybridized to oxygen.

Focusing on the spectral range from 1 eV to 4 eV, PCMO with a thickness of about 80 nm is a broadband absorber with a spectral absorptance of about 60%. The spectral dependence is discussed in more detail in [2,3]. The first absorption maximum, centered at about 1.6 eV, is due to transitions between non-bonding Mn3d $e_g$ and anti-bonding $\sigma$ type O2p-$e_g$ states [4], broadened by phonon-assisted processes and, towards low energy, by polaron hopping. Because of the disappearance of the JT splitting, this transition is not present in CMO. In addition to these near-infrared (NIR) features,
transitions between O2p and minority spin t2g /eg states dominate the absorption in the ultraviolet range above 2.5 eV [2].

In contrast to PCMO, the absorptance of CMO reveals an optical bandgap related to the charge transfer transition between O2p and Mn3d eg states. Extrapolating the almost linear decrease of $\alpha$ below 2 eV to zero-absorptance gives a band gap of about 1.3 eV, which is in accordance with the reported values in (e.g.[5]). Above 2 eV, the absorptance of PCMO and CMO are similar, they mainly differ in the NIR range.

The pristine STNO substrates reveal three different optical features:

i. A strong increase of the absorptance at about 3.2 eV, which is caused by interband transitions from O2p to Ti3d states across the band gap.

ii. A weak peak-like feature at about 2.4 eV. This transition is commonly related to some mid-gap states, probably caused by oxygen vacancies [6,7].

iii. A Drude-like increase of absorptance well below 2 eV. Since this feature systematically increases with the doping level of STNO [8], this additional absorptance is caused by intra-band quasi-particle excitations. Because of extremely small quasiparticle lifetimes, such excitations do not contribute to the photovoltaic effect.

All photovoltaic measurements presented below are performed under front side (manganite) illumination. With an optical penetration depth of 150-200 nm (90% drop of transmission) in the energy range between 1.5 and 3 eV, a possible contribution of the weak STNO absorption feature at 2.4 eV to the photo-voltaic effect is very small. In the spectral range below 2.3 eV, only photocarrier in the manganite contribute to the photovoltaic effect.

b) TEM investigations of heterojunctions

Structural properties and the chemical composition of the regions near the interface were investigated in an FEI Titan 80-300 keV G2 ETEM Transmission Electron Microscopy (TEM) system equipped with an Electron Energy Loss spectrometer (EELS) Gatan Quantum 965ER. Cross-sectional electron-transparent lamellas of the different heterojunctions were prepared via grinding and argon polishing using a Gatan 691 PIPS Precision Ion Polishing System.

PCMO films on STNO prepared by ion-beam sputtering reveal a predominant (001) orientation and a significant amount of (110) domains which evolve due to the cubic to orthorhombic phase transition and the resulting twinning. Post-annealing increases the size of the twin domains and leads to a vast annihilation of nano-sized disorder, e.g. local deviation of octahedral tilt. Growth, electrical and structural properties of these films are described in more detail in [9]. The manganite films are
typically highly strained, e.g., the out-of-plane strain of as-prepared films deduced from XRD amounts to about 1.3% and decreases with post-growth annealing.

Figure S2. Cross-sectional high-resolution ADF STEM images of the post-annealed PCMO/STNO (a) and the CMO/STNO junctions (c). White arrows indicate the location of the interface. Yellow dots and red arrows indicating the Burger’s circuits. EELS linescans of the PCMO/STNO (b) and CMO/STNO junction (d) reveal that cation interdiffusion is restricted to a 2.5 nm length scale. Antiphase boundaries with a CaO stacking fault can be observed in HAADF STEM and high resolution EELS mapping in the CMO films (e).

The stress-strain state is mainly governed by preparation-caused defects during the thin film deposition and relaxation of the lattice mismatch strain via dislocations plays only a minor role. Figure S2(a) shows an annular dark-field (ADF) image of the PCMO/STNO interface after additional
annealing. The interface is well-ordered and no extended defects are visible. However, misfit dislocations are located inside the STNO substrate. In as-prepared and post-growth annealed films, the dislocation density is of the order of \(1/\mu\text{m}^2\), see also \([10,11]\). Full relaxation of the lattice mismatch strain of about \(\Delta_{\text{STNO}} = -1.41\%\) would require a mean dislocation distance of about 29 nm, which implies that misfit relaxation via such dislocations is negligible.

In the ADF image, the chosen collection angle of 50-200 mrad gives rise to contrast which is sensitive to the atomic mass number. In figure S2(a) the sharp transition of the contrast at the interface implies that the intermixing of A and B site cations is small. At that range of scattering angles, coherent scattering additionally contributes to the ADF contrast. The additional diffuse bright contrast at the PCMO close to the interface is due to lattice disorder such as strain fields and maybe misfit relaxation by oxygen vacancies, as suggested by \([12]\).

As studied by EELS line scans across the PCMO/STNO interface (figure S2(b)), post-growth annealing does not lead to an increased interdiffusion of cations, compared to as prepared films studied in a former publication \([10]\). For the B-site cations, the sharpness of the interface is better than the resolution limit given by the excitation volume. It is estimated to about 1.5 nm. A slight asymmetric exchange of the Ca and Sr A-site cations is observed with an average interdiffusion length of 2.5 nm (figure S2(b)), shifting the A-site interface towards the STNO. A shift on a similar length scale was also observed in as-prepared PCMO films on STNO (figure 1 in \([10]\)) and is thus attributed to intermixing due to the impact of energetic particles involved in ion-beam sputtering.

TEM and XRD investigations of CMO films on STNO confirm the epitaxial growth. The major difference to the PCMO films is the presence of a high density of extended planar defects (figure S2(c)). We observe two types of anti-phase boundaries (APB) with shift vectors parallel and perpendicular to the boundary plane, and sometimes an additional CaO layer as a stacking fault (figure S2(e)). The latter can arise from surface steps of the STNO substrates. Without any additional surface treatment, STNO substrates show a mixed type of surface termination. In AFM investigations, we observe step heights of the atomic flat terraces of about one half and one unit cell of STNO. Similar to PCMO, the EELS line scan in figure S2(d) shows sharp B site concentration profiles being limited by the excitation volume of the electron beam. The interdiffusion length of the A-site cations is slightly above the resolution limit.

Summarizing the interface quality, the PCMO/STNO and the CMO/STNO junctions mainly differ in the appearance of APBs in the CMO which extend towards the CMO/STNO interface and may represent recombination active defects. The degree of intermixing is small for both types of interfaces.
c) Rectifying behavior of the manganite/titanite junctions

Figure S3. Current-voltage dependence of the different heterojunctions in the dark at 300K and 200K. All junctions show a rectifying behavior and a photovoltaic effect in the analyzed temperature region. With decreasing temperature the rectifying behavior getting more pronounced.

Figure S3 gives an overview on the current-voltage dependence of the different heterojunctions in the dark. All junctions reveal rectifying behavior, which is more pronounced at lower temperatures. Post annealing of PCMO/STNO improves the rectifying behavior. The diode-like shape of the $J$-$V$ curves is most pronounced for the CMO/STNO junctions.

d) References

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