

/LaAlO₃ (substrate) quantum wells near a polar surface of AlO₂-terminated LaAlO₃ (001). When the LaAlO₃ cap is thin, an exponential drop in resistance [Fig. 2(a)], a decreasing positive Seebeck coefficient [Fig. 2(b)], and loss of satellite diffraction streaks due to the LaAlO₃ surface reconstruction were observed below a characteristic coupling length of 10-15 unit cells (uc). We attribute this behavior to a crossover from an atomic reconstruction of the LaAlO₃ surface to an electronic one of the vanadium valence. A striking point is that the doped carriers are holes. This excludes the role of electron-donor oxygen vacancies, which make the origin of itinerant electrons at the LaAlO₃/SrTiO₃ interfaces controversial.

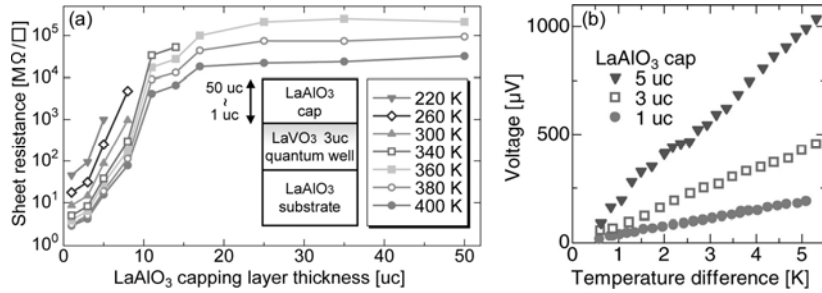


Fig. 2 (a) Sheet resistance of the LaVO₃ quantum well and (b) thermoelectric voltage induced to the quantum wells. Seebeck coefficient is the slope of this plot.

Changing interface compositions in LaAlO₃/SrTiO₃ superstructures

The metallic conductivity of LaAlO₃/SrTiO₃ strongly depends on the interface composition – inserting one monolayer of SrO in between makes the system insulating [b]. This can be understood with the polar discontinuity picture: switching the termination to SrO flips the sign of the compensation charge, resulting in excess positive charge, which can be realized by formation of oxygen vacancies, not itinerant holes. To further study this phenomenon, [LaAlO₃ (6 uc) / SrTiO₃ (12 uc)] × 7 superlattices were grown with different interface compositions. In the superlattices, we have two types of interfaces: LaAlO₃ above SrTiO₃ (L/S type), or the opposite (S/L). Unlike the previous works, a material with nominal composition of Sr₂Al₂O₅ (a mixture of Sr₃Al₂O₆ and SrAl₂O₄) was used to change the interface compositions in the superlattices without losing the *A* and *B* site cation number balance in the perovskites *ABO*₃. As shown in Fig. 3(a), a monolayer of Sr₂Al₂O₅ inserted at the L/S type interface made the system insulating, confirming the importance of L/S type interfaces in the metallic conduction. The atomic and electronic structures of the superlattices were studied by scanning transmission electron microscopy (STEM) equipped with electron energy loss spectroscopy (EELS) [Fig. 3(b, c)]. A clear signature of reduced Ti valence was observed only at the L/S interface, associated with deeper interdiffusion of the cations [Fig. 3(d)]. These observations were further supported by soft x-ray resonant scattering (SXRS) measurements. A model with 3 unit cells of interfacial layers only at L/S interfaces reproduced the SXRS data best. It is remarkable that the existence of interfacial layers were confirmed in both real space (STEM) and reciprocal space (SXRS), and the emergence of the novel properties were indeed produced by the change of the interface stoichiometry.

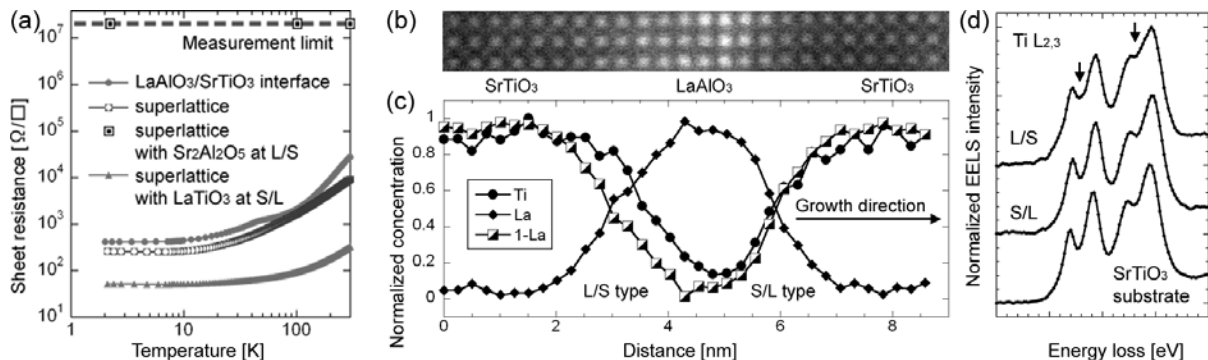


Fig. 3 (a) Sheet resistance of a single LaAlO₃/SrTiO₃ interface and superlattices with various interface compositions. (b) Annular dark field (ADF) STEM image and (c) concentration profile around LaAlO₃ (6 uc) in the LaAlO₃/SrTiO₃ superlattice. (d) EELS spectra showing the lower energy features (arrows) in the Ti L_{2,3} edge of the L/S type interface compared to the SrTiO₃ substrate and the S/L one, indicating the reduced valence [d].

Microscopic observations of LaMnO₃/SrTiO₃ interfaces

LaMnO₃/SrTiO₃ was chosen to further study the importance of the interface composition, due to its wide variability by inserting SrMnO₃. Unlike LaAlO₃/SrTiO₃, LaMnO₃/SrTiO₃ interfaces were insulating as grown, independent of the SrMnO₃ insertion (0 to 2 uc). The lack of conductivity even without SrMnO₃ was explained by the STEM-EELS observations of lower valence Mn (<3+), which do not contribute to the metallic transport. At the interface, the mixing of La and Sr was observed deeper into SrTiO₃ than that of Mn and Ti, suggesting the existence of La_xSr_{1-x}TiO₃ as the interface composition which provides the lower valence of Ti compared to that of SrTiO₃. These additional electrons in the Ti 3*d* states may prefer the Mn sites due to the lower energy of their 3*d*, hence explaining the Mn²⁺ features. As the inserted SrMnO₃ layers increased, the Mn²⁺ features decreased, suggesting the possible control of electronic states by changing interface compositions.

Summary

When there is a change in the dipole moment of the unit cells starting from the interface, the electrostatic potential diverges, and thus the ionic charges and stoichiometry cannot be maintained. This instability of polar discontinuities is equivalent to that the dipole free unit cell at the interface does not keep the stoichiometry of either bulk materials, even not a mere mixture of them. This issue is one of the central aims of this interface science of compounds. In transition metal oxides, due to the multi-valency, electronic reconstructions are available to reconcile the instability. Following these arguments, we describe three phenomena on changes of the electronic states at the nanoscale: modulation doping from a polar discontinuity, changing stacking sequence of two materials forming the interface, inserting other materials at the interface. These results provide general approach to tunable electronic states in oxide artificial structures.

* Other studies on the microscopic structure of the precipitates formed during PLD growth of LaMnO₃ [3], the photoluminescent properties of SrTiO₃ and related structures, and the fabrication of bright phosphor KVO₄:Eu(*R*=Y or La) thin films by PLD [6] are also presented in the Thesis.

References

- [a] P. W. Tasker, J. Phys. C: Solid State Phys. **12**, 4977 (1979).
- [b] A. Ohtomo and H. Y. Hwang, Nature (London) **427**, 423 (2004).
- [c] N. Nakagawa, H. Y. Hwang, D. A. Muller, Nature Materials **5**, 204 (2006).
- [d] See A. Ohtomo *et al.*, Nature (London) **419**, 378 (2002), and references therein.

Publications

- [1] T. Higuchi, Y. Hotta, T. Susaki, A. Fujimori, and H. Y. Hwang, "Modulation doping of a Mott quantum well by a proximate polar discontinuity," Phys. Rev. B, in press (selected as Editors' Suggestion).
- [2] H. Wadati, D. G. Hawthorn, J. Geck, T. Higuchi, Y. Hikita, H. Y. Hwang, S.-W. Huang, D. J. Huang, H.-J. Lin, C. Schüßler-Langeheine H.-H. Wu, E. Schierle, E. Weschke, and G. A. Sawatzky "Symmetry-Breaking Interface Reconstructions in SrTiO₃/LaAlO₃ Superlattices," submitted to Phys. Rev. Lett.
- [3] T. Higuchi, T. Yajima, L. Fitting Kourkoutis, Y. Hikita, N. Nakagawa, D. A. Muller and H. Y. Hwang, "Atomic and Electronic Structure of Mn₃O₄ Precipitates in Laser-Ablated Manganite Films," in preparation.

* Two more activity reports as a coauthor (CLS, Canada and NSRRC, Taiwan).

Presentations (selected)

- [4] T. Higuchi, Y. Hotta, T. Susaki, A. Fujimori, and H. Y. Hwang, "Tunable carrier injection into LaVO₃ Mott quantum wells by coupling to a proximate polar surface reconstruction," CERC International Symposium 040 (2007).
- [5] T. Higuchi, Y. Hotta, T. Susaki, A. Fujimori, and H. Y. Hwang, "Modulation doping of a vanadate Mott quantum well by a proximate polar discontinuity," JSAP 55th Spring meeting, 29p-L-1 (2008) (invited).
- [6] T. Higuchi, Y. Hotta, Y. Hikita, L. Fitting Kourkoutis, S. Maruyama, D. A. Muller, H. Akiyama, and H. Y. Hwang, "Bright phosphor KVO₄:Eu(*R*=Y, La) thin films by pulsed laser deposition," to be presented at JSAP 56th Spring meeting (2009).

* Seven presentations as the first author and fourteen presentations as a coauthor in total.

Awards

- [7] T. Higuchi, "Japan Society of Applied Physics, the 23rd Encouraging Prize for the Presentations" (2008).

* Two more poster presentation awards (52nd and 53rd Summer Schools of Condensed Matter Physics).