研究課題別評価

１　研究課題名： Correlated Electron Optics in Quantum Confined Mott Insulators

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３　研究のねらい：

A diverse range of physical properties can be found in perovskite oxides closely latticed-matched to one another. Our general research interest is to develop these materials as a new heteroepitaxial family with new physical phenomena and devices, focusing on atomic scale control and design. When we consider basic artificial structures used in semiconductor devices, such as heterojunctions and quantum wells, we find two important issues arise when incorporating perovskites: 1) *The atomic composition of the interface.* For abrupt perovskite interfaces in the (001) orientation, there are two different interface terminations which can be grown with often vastly different electronic properties. 2) *Incorporating strongly correlated electrons.* A key feature for poorly screened electrons is that the electronic structure evolves with electron density, quite different from filling electrons into a rigid single particle band. The aim this project was to develop the materials ingredients and optical probes for using band bending and quantum confinement with correlated electrons in perovskite oxide heterostructures.

４　研究成果：

Modulation of oxygen stoichiometry on an atomic scale

The electronic properties of $SrTiO_3$ are extremely sensitive to oxygen stroichiometry – the evolution from a dielectric insulator, to a doped semiconductor, then to a metal and superconductor all occurs within the first 0.03 % of oxygen vacancies. We have studied the growth dynamics and electronic properties of $SrTiO_{3-\delta}$ homoepitaxial films by pulsed laser deposition. We find the two dominant factors determining the growth mode are the kinetics of surface crystallization and oxidation. When matched, persistent two-dimensional layer-by-layer growth can be obtained for hundreds of unit cells. By tuning these kinetic factors, oxygen vacancies can be frozen in the film, allowing controlled, systematic doping across a metal-insulator transition. By varying the oxygen partial pressure during growth, we could fabricate $SrTiO_3/SrTiO_{3-\delta}$ superlattices with oxygen doping profiles exhibiting sub-nanometer abruptness. Using annular-dark-field electron microscopy and core-level spectroscopy, we were for the first time able to profile realistic vacancy concentrations on an atomic scale. This opens a pathway to the microscopic study of individual vacancies and their clustering.

Manipulating Interface States Using Polar Discontinuities

The electronic structure of perovskite interfaces can be dramatically tuned at the atomic level. We examined the (001) interface between two insulators, $SrTiO_3$ (composed of charge neutral layers) and $LaAlO_3$ (composed of alternatively charged layers). This 'polar discontinuity' creates a diverging potential, which forces an *electronic reconstruction* for n-type interfaces, and an *atomic reconstruction* for p-type interfaces. The n-type interface forms an artificial high-mobility metallic state at the interface between two insulators. Although polar discontinuities are a unique approach to creating novel interface states, it is also valuable to create oxide heterostructures with electrically clean interfaces. Towards this end, we note that in the (110) orientation, the interface should be free of interface states for all perovskite combinations. We have found a unique two stage annealing procedure which gives an atomically flat (110) $SrTiO_3$ surface, while maintaining an insulating surface. We have demonstrated two-dimensional layer-by-layer homoepitaxial and heteroepitaxy growth in this new growth orientation.

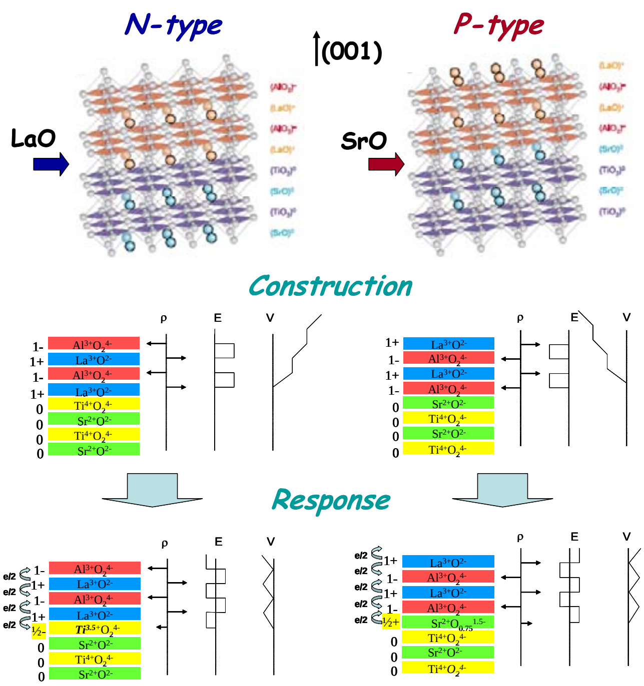

Fig. 1. The two (001) interfaces between $LaAlO_3$ and $SrTiO_3$. The unreconstructed interface has a polar discontinuity, leading to a potential divergence. This is resolved by an electronic reconstruction in the n-type case (induced Ti^{3+}), and an atomic reconstruction in the p-type case (induced oxygen vacancies).

Artificial Structures Incorporating the Mott Insulator $LaVO_3$

A central focus of this project has been to develop $LaVO_3$ as a perovskite component in thin film heteroepitaxial structures. $LaVO_3$ is a prototypical Mott insulator showing a large correlation gap (>1 eV), with a spin and orbital ordered ground state. The thin film growth phase diagram evolves between $LaV^{3+}O_3$ and $LaV^{5+}O_4$ with varying thermodynamic conditions. Between these phases lies an extended region of phase coexistence, since $LaV^{4+}O_x$ cannot form in bulk. In this regime we have examined abrupt interfaces between $LaV^{3+}O_3$ and $LaV^{5+}O_4$, and we find the vanadium valence smoothly varies from V^{3+} to V^{5+}, inducing a nanometer wide region of V^{4+} at the interface. This is a striking example of the strong electronic reconstructions which can occur at transition metal oxide interfaces. For optimized conditions, atomically flat $LaVO_3$ films can be grown in the layer-by-layer growth mode, and we have successfully fabricated superlattices of $LaVO_3/SrTiO_3$ and $LaVO_3/LaAlO_3$ down to single unit cell layers. In the latter case, we have examined the electronic structure of the $LaVO_3$ Mott quantum wells using x-ray photoemission spectroscopy. We have found that the well can be systematically doped by charge transfer from the polar $LaAlO_3$ surface. Studies of the optical properties of these quantum wells are in progress, and preliminary results indicate that for ultra-thin wells, the reduced dimensionality increases the bandgap and reduces the bandwidth of the upper Hubbard band.

Magnetically Tunable Interface Barrier in Manganite/Titanate Heterojunctions

We have studied rectifying Schottky junctions using ferromagnetic manganite electrodes. For high T_C manganites such as $La_{0.7}Sr_{0.3}MnO_3$, there is little magnetic field dependence at all temperatures. However, for manganites near the metal-insulator transition, such as $La_{0.7}Sr_{0.3}MnO_{3-\delta}$, the junction exhibits a magnetic field tunable depletion layer. This creates a large positive magnetocapacitance, a direct measure of the field-induced reduction of the effective depletion width across the junction. Furthermore, the reduction of the junction barrier shifts the forward bias characteristics, giving exponentially-enhanced differential magnetoresistance, occurring despite the absence of a spin filter. These results provide a unique probe of a Mott insulator/band insulator interface. They further suggest the potential for creating new electronic devices incorporating the magnetic field sensitivity of these strongly correlated electron materials. To probe the origin of this effect, we have developed a probe to use internal photoemission spectroscopy under magnetic field. This technique can directly measure the Schottky barrier height by monitoring the photocurrent across the junction while illuminated by tunable monochromatic light. We find that the barrier height can be significantly reduced by magnetic field, consistent with the electronic properties. This result, opposite of what would be expected from purely Zeeman effects, may indicate an interface metal-insulator transition driven by magnetic field.

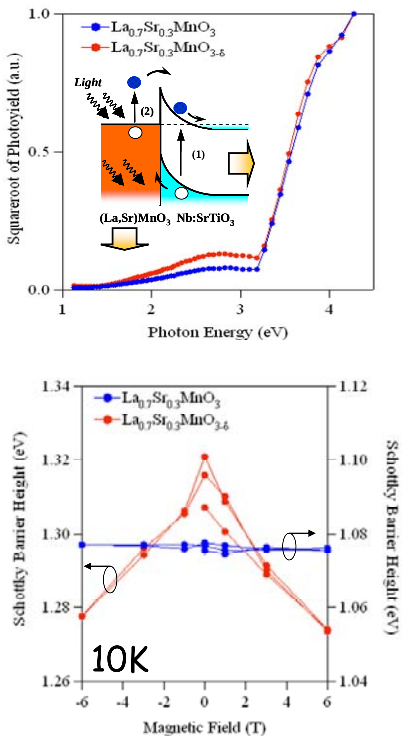

Fig. 2. The top panel shows the photocurrent yield as a function of photon energy. The two principle features observed are the $SrTiO_3$ bandgap and the Schottky barrier height. The bottom panel shows the evolution of the barrier height with applied magnetic field. Only the magnetically active $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ junction exhibits field dependence.

5　自己評価：

We have studied perovskite oxide thin films, interfaces, and multilayers with the general aim of developing complex oxide heteroepitaxial structures with new physical properties and device potential. At $LaAlO_3/SrTiO_3$ and $LaVO_3/LaVO_4$ interfaces, we have found nanometer scale interface phases driven by electronic reconstructions. At manganite/titanate rectifying interfaces, we have found the barrier height can be strongly reduced by applied magnetic field, which we directly probe using internal photoemission spectroscopy. Having developed atomically precise structures incorporating the Mott insulator $LaVO_3$, we have begun to probe the electronic structure of quantum-confined correlated electron states. We are proceeding to probe the linear and nonlinear optical response of these structures, analogous to semiconductor multiple quantum wells. In our view, the development of new materials structures and interface phenomena has been highly successful in this project. However, we have been slow to investigate and develop the optical probes and properties of our structures, with significant progress occurring only in the last year of this project. In summary, this should be a promising new direction for manipulating the many bulk physical properties associated with heterovalent transition metal oxides, applying the concept of bandgap engineering in perovskite heterostructures. In addition to a number of scientific accomplishments within this project, we believe this research has seeded several exciting new research concepts and directions, which we will continue to pursue in future research.

6　研究総括の見解：

高速電子線回析で観測しながらレーザーアブレーションを実行し、強相関電子系のヘテロ構造を原子層単位で積み上げることに成功した。その結果として第一に、二つの絶縁体$SrTiO_3$と$LaAlO_3$のヘテロ界面は、積層面の組み合わせによりn型とp型の二種類が出来て、特にn型のヘテロ界面では二次元高移動度金属状態が形成することを発見した。第二として、モット絶縁体$LaVO_3$と $LaAlO_3$の界面での電子構造が再構築される様子を光学測定で観測し、第三に、(La、Sr)MnO_3とNb：$SrTiO_3$のショトキーバリヤーにおける光励起で生成した電子・正孔対のダイナミックスと ショトキーバリヤー壁の高さの磁場による変動を明らかにした。

これらのヘテロ構造の作製法の飛躍的進歩とその電子構造の解明は、強相関電子系を用いた光デバイスの作製可能性を示唆し、更なる発展が極めて楽しみである。

7　主な論文等：

論文(18 件)

1. Y. Hotta, H. Wadati, A. Fujimori, T. Susaki, and H. Y. Hwang, "Electronic Structure of the Mott Insulator $LaVO_3$ in a Quantum-Well Geometry," *Applied Physics Letters*, **89**,251916(2006)
2. N. Nakagawa, H. Y. Hwang, and D. A. Muller, "Why Some Interfaces Cannot be Sharp," *Nature*

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3. N. Nakagawa, M. Asai, Y. Mukunoki, T. Susaki, and H. Y. Hwang, "Magnetocapacitance and Exponential Magnetoresistance in Manganite-Titanate Heterojunctions," *Applied Physics Letters* **86**, 082504 (2005).
4. D. A. Muller, N. Nakagawa, A. Ohtomo, J. L. Grazul, and H. Y. Hwang, "Atomic-scale Imaging of Nanoengineered Oxygen Vacancy Profiles in $SrTiO_3$," *Nature* **430**, 657 (2004).
5. A. Ohtomo and H. Y. Hwang, "A High-Mobility Electron Gas at the $LaAlO_3/SrTiO_3$ Heterointerface," *Nature* **427**, 423 (2004).

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特許(2 件)

1. 特願 2004-252805 号(特開 2006-069820 号)「酸化物結晶の処理方法及び酸化物結晶」、
平成 16 年 8 月 31 日出願(平成 18 年 3 月 16 日公開)、
H. Y. Hwang、椋木康滋、中川直之、須崎友文
2. 特願 2004-252809 号(特開 2006-073629 号)「ヘテロ接合素子、ヘテロ接合モジュール、及びヘテロ接合素子の制御方法」、
平成 16 年 8 月 31 日出願(平成 18 年 3 月 16 日公開)、
H. Y. Hwang、中川直之、浅井雅司、須崎友文

受賞(1 件)

表彰年月日：平成17年3月30日

2005 Materials Research Society Outstanding Young Investigator Award

(米国材料学会若手優秀研究者賞)

受賞理由：「For innovative work on the materials physics of transition metal oxides and the atomic-scale synthesis of complex oxide heterostructures」

招待講演(18 件)

1. H. Y. Hwang, "Chemistry of Oxide Heterointerfaces on the Atomic Scale," Kyoto Conference on Solid State Chemistry: Transition Metal Oxides - Past, Present and Future, Kyoto, Japan, November 14-18, 2006.
2. H. Y. Hwang, "Magnetic Field Control of the Interface in Manganite-Titanate Heterojunctions," International Conference on Physics Near the Mott Transition, Indian Institute of Science, Bangalore, India, July 24-28, 2006.
3. H. Y. Hwang, "Atomic Control of the Electronic Structure at Complex Oxide Heterointerfaces," 2005 Outstanding Young Investigator Award Presentation, Materials Research Society Spring Meeting, San Francisco, CA, March 28-April 1, 2005.
4. H. Y. Hwang, "Electronic Structure at Mott Insulator/Band Insulator Interfaces," American

Physical Society March Meeting, Los Angeles, CA, March 22–26, 2005.

5. H. Y. Hwang, "Strongly Correlated Electrons at Artificial Interfaces and in Confined Systems," Japan Physical Society Fall Meeting, Aomori, Japan, September 12–15, 2004.

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