科学研究費補助金研究成果報告書

平成 21 年 6 月 3 日現在

研究種目:基盤研究(B)				
研究期間:2007~2008				
課題番号:19340094				
研究課題名(和文)	ナノスケール酸化物における電界誘起相転移			
研究課題名(英文)	Field effect phase transitions in nanoscale oxides			
研究代表者 リップマー ミック(Lippmaa, Mikk) 東京大学・物性研究所・准教授 研究者番号:10334343				

研究成果の概要:

We have developed a process for fabricating micron-scale fully epitaxial top-gate oxide field-effect transistors that use an oxide channel, oxide source and drain electrodes and a wide-gap oxide gate insulator. We have studied charge accumulation at CaHfO₃/SrTiO₃, DyScO₃/SrTiO₃, and SrTiO₃/LaTiO₃ interfaces. As a way to confine carriers in a narrower layer at an interface, we are developing Ruddlesden-Popper-type two-dimensional quantum wells.

交付額

			(金額単位:円)
	直接経費	間接経費	合 計
2007 年度	8,100,000	2,430,000	10,530,000
2008 年度	6,400,000	1,920,000	8,320,000
年度			
年度			
年度			
総計	14,500,000	4,350,000	18,850,000

研究分野:数物系科学 科研費の分科・細目:物理学・物性 キーワード:電子デバイス・機器、ナノ材料、表面・界面物性、物性実験

1.研究開始当初の背景

Many oxides have very rich electronic phase diagrams with various insulating, metallic, magnetic, superconducting, etc. phases. In many materials, these phase transitions can be controlled by changing the density of charge carriers, i.e. doping. A particularly attractive method of doping oxide is to use the electrostatic field effect to tune the carrier density in a two-dimensional layer continuously over a phase transition.

2.研究の目的

The purpose of the project was to study the possibility of observing phase transitions in $SrTiO_3$ and other oxides by constructing fully epitaxial field effect transistors, in which the carrier density in the transistor channel can be adjusted by simply

changing the gate voltage. Since the carrier density modulation range is limited by the breakdown field of the insulator, our purpose was to study phase transitions that occur at moderately low carrier densities, such as the insulator-metal and insulator-superconductor transition in SrTiO₃. Of particular interest for us was the possibility of controlling localization-driven insulator-metal transitions in two-dimensional oxide layers.

3.研究の方法

We used laser molecular beam epitaxy to grow high-quality fully epitaxial oxide heterostructures consisting of SrTiO₃ and several different insulator materials (CaHfO₃ and DyScO₃) and different channel compositions (SrTiO₃, oxygendeficient SrTiO₃, (La,Sr)TiO₃, and various Ruddlesden-Popper type manganites. The heterostructures were patterned by photolithography and ion milling. Transistor electrodes consisting of metallic oxygen-deficient SrTiO₃ were also made by ion milling. The transport properties of the field-effect transistors and magnetotransport of heterostructures were measured as a function of temperature, carrier density, magnetic field, and ultraviolet illumination. The occurrence of metal-insulator transitions was observed.

4.研究成果

(1) We developed a process for fabricating epitaxial field-effect transistors based on epitaxial oxide layers (Fig. 1). This device structure can be used to study the transport properties of various ultrathin oxide layers that can be grown on SrTiO₃. The best performance is generally obtained in the smallest devices, which are less affected by defects in the films.



Fig. 1 Array of transistors with various channel sizes.

(2) A technique was developed to use oxygen-deficient $SrTiO_3$ as an electrode material for epitaxial oxide FETs (Fig. 2). A key feature of this design is that the

channel interface layer can be grown before any other device processing or patterning. In this way, the best channel interface quality can be obtained.



Fig. 2 Cross-sectional view and optical image of an oxide transistor.

(3) The SrTiO₃-based oxide FETs were used in depletion mode for mapping the density of in-gap states at the SrTiO₃/DyScO₃ interface. The variation of



Fig. 3 Schematic diagram of in-gap states near SrTiO3 conduction band and measured density of states.

the activation energy of channel conductance as a function of gate bias, or quasi-Fermi level distance from the conduction band mobility edge, shows plateau-like behavior about 400 meV below the conduction band bottom (Fig. 3). This result was obtained in a slightly oxygen-deficient crystal, showing that simple transport measurements in an FET can provide electronic density information that would normally require synchrotron source photoelectron emission spectroscopy measurements. Additionally, the FET measurements probe the electronic density in an essentially two-dimensional interface layer, which is generally not accessible in photoemission experiments.

(4) The ability to induce a large enough carrier density at an interface to observe phase transitions in common oxide systems, is limited by the breakdown of the insulator and trapping of charge at interfaces. Charge trapping is also the basis for some types of resistive switching devices that have been proposed as new high-density non-volatile memories. Charge trapping at various interfaces in an device can oxide be studied bv capacitance-voltage analysis (insulator layers) and by measuring the temperature dependence of the transistor switching characteristics (channel material). Since the mobility of charge carriers in SrTiO₃ is strong function of temperature, а measuring low-temperature the performance of an FET can clearly show if interface traps (and thus defects) remain at the channel interface. An example of such a measurement is shown in Fig. 4.



Fig. 4 Temperature dependence of $SrTiO_3$ / $DyScO_3$ FET switching characteristics.

The data in Fig. 4 shows that the off-current of the device drops exponentially with temperature. This is caused by in-gap defect states in SrTiO₃, assigned mostly to oxygen defects. The increase of the slope of the switching curves at low temperature shows that the mobility increases at low temperature, as expected for SrTiO₃.



(5) The mobility behavior of a FET is a good probe of interface quality in an electronic sense. The field-effect mobility measured in a 10 μ m channel length device is overlaid on bulk mobility data for SrTiO₃ in Fig. 5. This type of measurement sees

the average mobility in the channel region and is generally lower than the bulk mobility. For the particular device for which the data is shown in Fig. 5, it is clear that the mobility does follow the bulk characteristics and it can be concluded that epitaxial oxide interfaces can be grown with sufficiently low impurity or structural defect densities. This is important if we consider an FET as a general tool for measuring electronic phase diagrams in nm-scale oxide layers.

(6) We have observed metal- superconductor and metal-insulator transitions in oxide FETs and related structures. The main benefit of an FET as an electronic doping tool is that the electron density can be changed reversibly, and with much better accuracy than is possible by chemical doping. It is therefore possible to study the effects of small perturbances caused by changes in temperature, magnetic fields, light, etc. on a material at the 'midpoint' of a phase transition. A metal-insulator transition measured in a SrTiO₃ FET is illustrated in Fig. 6.

The data in Fig. 6 shows how the sheet



resistance behavior vs. temperature changes as the electric field is varied between 0.8 and 1.3 MV/cm. The maximum field in this case corresponds to a sheet carrier density increase of about $5x10^{12}$ cm⁻². Considering that for bulk SrTiO₃, the transition occurs at a carrier density of about $5x10^{17}$ cm⁻³, it is evident that the conducting channel thickness is on the order of at least tens of nm.

(7) The thickness of a conducting layer at an oxide heterointerface is determined by the depth distribution of defects and the dielectric properties of the material. In the materials studied in this project, it is important to consider the motion of oxygen vacancies, which can have very high mobilities at typical thin film growth temperatures of about 700 °C. In order to confine carriers in a thinner interface layer and thus achieve higher volume densities of carriers, it is necessary to restrict the movement of either cation or anion defects and electrons. One possible approach is to use rocksalt-type layers to isolate perovskite layers from the rest of the crystal, i.e. a structure similar to a unit cell of a Ruddlesden-Popper phase.



Fig. 7 shows the specular intensity oscillations during laser molecular beam epitaxy growth of a three unit cell thick film of $(La,Sr)_3(Mn,Ru)_2O_7$. The data shows that it is possible to determine exactly which crystal blocks grow on the surface and the layer sequence can be changed by growing a film a single block at a time, using separate *A* and *B*-site cation targets.

(8) In order to achieve tighter electron confinement, we have studied this in SrTiO₃ / LaTiO₃ / SrTiO₃ trilayer structures, where the LaTiO₃ layer coverage is less than 1 full unit cell. This type of a fractional-layer quantum well shows string localization and a transition from a metallic or semiconducting state to an insulating state at about 100 K. The temperature dependence of resistivity of fractional-layer LaTiO₃ quantum wells is shown in Fig. 8. LaTiO₃ layers that are close to 1 unit cell thick, are metallic. At a coverage of about 0.2 unit cells, a sharp transition to insulating state is seen at about 50 K. This type of well structures can also be used for doping studies in FET structures, since the quantum wells can easily be integrated in the FET channel.





- 5.主な発表論文等
- 〔雑誌論文〕(計14件)
- 1. M. Matvejeff, T. Chikyow and <u>M.</u> <u>Lippmaa</u>, "Interface growth of La_{1.2}Sr_{1.8}Mn_{1.7}Ru_{0.3}O₇ Ruddlesden-Popper films on SrTiO₃:, J. Cryst. Growth 311 (2009) 1201-1205, 査読有.
- 2. K. Shibuya, <u>T. Ohnishi</u>, T. Uozumi, T. Sato, K. Nishio and <u>M. Lippmaa</u>, "Observation of SrTiO3 in-gap states by depletion mode field effect", Appl. Phys. Lett., 92 (2008) 32109(1-3), 査読有.
- I. Ohkubo, K. Tsubouchi, T. Harada, H. Kumigashira, K. Itaka, Y. Matsumoto, <u>T. Ohnishi, M. Lippmaa</u>, H. Koinuma and M. Oshima, "Field-induced resistance switching at metal/perovskite manganese oxide interface", Mat. Sci. Eng. B 148 (2008) 13-15, 査読有.
- 4. <u>大西 剛</u>, パルスレーザー堆積法による 複酸化物薄膜のエピタキシー, 機能性材料 28 (2008) 6-14, 査読無.
- 5. T. Harada, I. Ohkubo, K. Tsubouchi, H. Kumigashira, T. Ohnishi, <u>M. Lippmaa</u>, Y. Matsumoto, H. Koinuma and M. Oshima, "Trap- controlled space- charge- limited current mechanism in resistance switching at Al/Pr0.7Ca0.3-MnO3 interface: Appl. Phys. Lett. 92 (2008) 222113(1-3), 查読有.
- 6. H. Kumigashira, M. Minohara, M. Takizawa, A. Fujimori, D. Toyota, I. Ohkubo, M. Oshima, M. Lippmaa and M. Kawasaki, "Interfacial electronic structure of SrTiO₃ SrRuO₃ heterojuctions studied in situ by photoemission spectroscopy", Appl. Phys. Lett. 92 (2008) 122105 (1-3), 查読有.
- 7. <u>T. Ohnishi</u>, K. Shibuya, T. Yamamoto and <u>M. Lippmaa</u>, "Defects and transport in complex oxide thin films", J. Appl. Phys. 103 (2008) 103703(1-6), 査読有.
- 8. K. Shibuya, <u>T. Ohnishi</u>, T. Sato and <u>M.</u> <u>Lippmaa</u>, "Metal-insulator transition in

SrTiO₃ induced by field effect", J. Appl. Phys. 102 (2007) 083713(1-4), 查読有.

- 9. <u>T. Ohnishi</u>, T. Yamamoto, S. Meguro, H. Koinuma and <u>M. Lippmaa</u>, "Pulsed laser ablation and deposition of complex oxides", J. Phys: Conf. Ser. 59 (2007) 514-519, 査読有.
- 10. K. Tsubouchi, I. Ohkubo, H. Kumigashira, M. Oshima, Y. Matsumoto, K. Itaka, T. Ohnishi, M. Lippmaa and H. "High-Koinuma, throughput characterization of metal electrode performance for electric- field-induced switching metal/ resistance in Pr0.7Ca0.3MnO3/ metal struc- tures", Adv. Mat. 19 (2007) 1711-1713 杳読有.
- 11. <u>大西 剛</u>、<u>M. Lippmaa</u>,酸化物薄膜成長 中の RHEED 強度振動,表面科学 28 (2007) 223-226,査読無.
- 12. K. Shibuya, T. Ohnishi, M. Lippmaa and M. Oshima, "Metallic conductivity at the CaHfO₃/SrTiO₃ interface", Appl. Phys. Lett. 91 (2007) 232106(1-3), 查読有.
- 13. T. Sato, K. Shibuya, <u>T. Ohnishi</u>, K. Nishio and <u>M. Lippmaa</u>, "Fabrication of SrTiO₃ field effect transistors with SrTiO₃₋₆ source and drain electrodes", Jpn. J. Appl. Phys. 46 (2007) L515-L518, 查読有.
- 14. H. Kumigashira, R. Hashimoto, A. Chikamatsu, M. Oshima, H. Wadati, A. Fujimori, M. Lippmaa, M. Kawasaki and H. Koinuma, "In situ photoemission characterization of the tunneling barrier La0.6Sr0.4MnO3 SrTiO3 in / - / La0.6Sr0.4MnO3 tunneling junctions", J. Magn. Magn. Mater. 310 (2007)1997-1999, 査読有.

[学会発表](計29件)

- <u>大西</u> 剛, <u>Mikk Lippmaa</u>, SrTiO₃の表 面・界面電子伝導:2 層伝導モデル,第56 回応用物理学関係連合講演会2009.3.30-4.2 (筑波大)
- 伊高健治, Lippmaa Mikk, 大西 剛, 片山正士,知京豊裕,鯉沼秀臣,フレキシブ ル真空搬送機構を備えた超小型モジュール 型薄膜・評価作製システムの開発,第56回 応用物理学関係連合講演会 2009.3.30-4.2 (筑波大)
- 大塚怜奈,西尾和記,ミッコマトヴィ エフ,<u>ミックリップマー</u>,SrTiO3にはさま れた極薄LaTiO3層における輸送特性,第 56回応用物理学関係連合講演会 2009.3.30-4.2(筑波大)
- 4. 菊月達也,<u>大西 剛</u>,<u>ミック リップマ</u> <u>ー</u>,VO2 薄膜における歪みを利用した相転

移現象, 第 56 回応用物理学関係連合講演会 2009.3.30-4.2 (筑波大)

- 5. 西尾和記, 安部拓也, <u>ミック リップマ</u> <u>-</u>, DyScO₃/SrTiO₃界面の電気伝導特性, 第 56 回応用物理学関係連合講演会 2009.3.30-4.2 (筑波大)
- 6. M. Matvejeff, T. Chikyow, <u>M. Lippmaa</u>, "Growth of (ultra) thin La_{1.2}Sr_{1.8}Mn_{1.7}Ru_{0.3}O₇ Ruddlesden-Popper films on (SrO buffered) SrTiO₃", 15th Workshop on Oxide Electronics, 14-17.9.2008, Estes Park, USA
- 7. K. Nishio, T. Abe, <u>T. Ohnishi, M.</u> <u>Lippmaa</u>, "Single Crystal SrTiO₃ (100) Field Effect Transistors with epitaxial DyScO₃ gate insulator", 15th Workshop on Oxide Electronics, 14-17.9.2008, Estes Park, USA
- 8. 小塚裕介, <u>大西</u> 剛, <u>Mikk Lippmaa</u>, 疋田育之, Harold Hwang, パルスレーザー 堆積法による低濃度キャリアドープされた 高移動度 n 型 SrTiO₃ 薄膜の作製, 第 69 回 応用物理学会学術講演会 2008.9.2-5(中部 大)
- 9. 安部拓也,西尾和記,<u>大西 剛</u>,<u>ミック</u> <u>リップマー</u>,界面層が DyScO₃ キャパシタ の誘電特性に及ぼす影響,第 69 回応用物理 学会学術講演会 2008.9.2-5(中部大)
- 10. 西尾和記, 安部拓也, 大西 剛, ミック リップマー, 単結晶 SrTiO3 電界効果トラ ンジスタにおける電流の緩和現象, 第 69 回 応用物理学会学術講演会 2008.9.2-5(中部 大)
- 西尾和記,安部拓也,佐藤泰輔,魚住嵩 之,渋谷圭介,<u>大西 剛,リップマーミッ</u> <u>ク</u>,ディプリーション型電界効果トランジ スタによる SrTiO₃ バンド間準位の評価,第 5 5 回応用物理学関係連合講演会 2008.3.27-30 日本大学
- 13. 菅野弦哉,原田尚之,大久保勇男,組頭 広志,<u>大西</u>剛,松本祐司<u>Mikk Lippmaa</u>, 鯉沼秀臣,尾嶋正治,人工界面酸化物層を導 入した金属/Pro.7Cao.3MnO3界面の電流-電 圧特性,第55回応用物理学関係連合講演 会 2008.3.27-30 日本大学
- 14. <u>大西</u> 剛,花宮英美,道間健一,<u>Mikk</u> <u>Lippmaa.</u>Pulsed Laser Deposition : SrTiO₃ 導電層の形成と評価,第55回応用 物理学関係連合講演会 2008.3.27-30 日 本大学
- 15. <u>大西</u> 剛, 望月圭介, 山本博文, 藤本英 司, 角谷正友, <u>Mikk Lippmaa</u>, SrTiO3の

発光, 第55回応用物理学関係連合講演会 2008.3.27-30 日本大学

- 16. <u>T. Ohnishi</u>, T. Yamamoto, <u>M. Lippmaa</u>, Composition modulated homoepitaxial superlattices of SrTiO₃, 14th Workshop on Oxide Electronics, Oct. 7-10, 2007, Jeju, Korea
- 17. Y. Urata, <u>T.Ohnishi</u>, H. Yamamoto, T. Ishii, S. Kawaminami, <u>M.Lippmaa</u>, <u>"Photoconductivity of defect-rich SrTiO₃</u> single crystals", 14th Workshop on Oxide Electronics, Oct. 7-10, 2007, Jeju, Korea
- 18. K. Nishio, T.Abe. <u>T.Ohnishi</u>, <u>M.Lippmaa</u>, "Scaling of single crystal SrTiO₃ (100) field effect transistors", 14th Workshop on Oxide Electronics, Oct. 7-10, 2007, Jeju, Korea
- 19. <u>M. Lippmaa</u>, K. Nishio, <u>T. Ohnishi</u>, K. Shibuya, "Field effect-driven insulatormetal transition in SrTiO₃", 14th Workshop on Oxide Electronics, Oct. 7-10, 2007, Jeju, Korea
- 20. R. Sakai, <u>T. Ohnishi</u>, N. Shibata, T. Mizoguchi, Y. Ikuhara, T, Yamamoto, "Control of A/B ratio in ABO₃ perovskite oxides by pulsed laser deposition", 14th Workshop on Oxide Electronics, Oct. 7-10, 2007, Jeju, Korea
- 21. T. Harada, I. Ohkubo, H. Kumigashira, <u>T. Ohnishi, M. Lippmaa</u> M. Katayama, Y. Matsumoto, H. Koinuma, M. Oshima, "Effects of metal electrodes on I-V characteristics of metal/perovskite manganite Schottky contacts", 14th Workshop on Oxide Electronics, Oct. 7-10, 2007, Jeju, Korea
- 22. E. Kawase, <u>T. Ohnishi</u>, S.-Y.Choi, T. Mizoguchi, N. Shibata, Y. Ikuhara, T. Yamamoto, "Control of surface step structure of $SrTiO_3$ (100) substrate by dopant", 14th Workshop on Oxide Electronics, Oct. 7-10, 2007, Jeju, Korea
- 23. 西尾和記, 安部拓也, <u>大西</u> 剛, 山本剛 久, <u>Mikk Lippmaa</u>, 単結晶 SrTiO3 電界効 果トランジスタに向けたエピタキシャル DyScO3薄膜の作製, 第68回応用物理学会 学術講演会 2007.9.4-8 北海道工業大学
- 24. <u>大西</u>剛,望月圭介,米澤卓三,上殿明 良,<u>Mikk Lippmaa</u>, SrTiO₃の色,第68回 応用物理学会学術講演会 2007.9.4-8 北 海道工業大学
- 大西 剛, <u>Mikk Lippmaa</u>, Pulsed Laser Deposition:酸化物ターゲット中の酸素第
 8回応用物理学会学術講演会 2007.9.4-8 北海道工業大学
- 26. 浦田康文 ,<u>大西 剛</u> ,山本博文 ,石井 誉 , 川南修一 ,<u>Mikk Lippmaa</u>,格子欠陥のある

SrTiO3 の光励起電気伝導特性,第68回応 用物理学会学術講演会 2007.9.4-8 北海 道工業大学

- Mikk Lippmaa, 大西 剛, 西尾和記, 安部拓也, 単結晶 SrTiO3 電界効果トランジ スタに向けた DyScO3 薄膜の低温誘電特性, 第68回応用物理学会学術講演会 2007.9.4-8 北海道工業大学
- 28. H. Wadati, A. Maniwa, I. Ohkubo, H. Kumigashira, A. Fujimori, M. Oshima, <u>M. Lippmaa</u>, M. Kawasaki and H. Koinuma, "In-situ photoemission study of $Pr_{1-x}Ca_xMnO_3$ epitaxial thin films", 2007 CERC International Symposium, Akihabara 2007.5.22-25
- 29. <u>M. Lippmaa</u>, "Oxide hetero- structures for field-effect devices", Materials Research Society, 4月9-13日、2007, San Francisco, USA

〔図書〕(計1件)

1. B. Posadas, <u>M. Lippmaa</u>, F. J. Walker, M. Dawber, C. H. Ahn and J. -M. Triscone, "Growth and novel applications of epitaxial oxide thin films", in: Physics of Ferroelectrics: A Modern Perspective, Topics in Applied Physics 105, edited by J.-M. Triscone, C. H. Ahn, K. M. Rabe, (Springer-Verlag, Berlin, 2007), 219-304, 査読無.

〔産業財産権〕

取得状況(計2件)

1. 角谷 正友,藤本 英司,渡邊 賢司,<u>ミック リップマー,大西 剛,</u>鯉沼 秀臣,酸 化亜鉛薄膜の形成方法,2008-244 011,公開日 2008.10.9 2. 角谷 正友,<u>ミック リップマー,大西</u> 剛,藤本 英司,鯉沼 秀臣,真空プロセス 用装置,2008-25017,公開日 2008.2.7

6.研究組織
(1)研究代表者
リップマー ミック(Lippmaa, Mikk)
東京大学・物性研究所・准教授
研究者番号:10334343
(2)研究分担者
(3)連携研究者
大西 剛(Ohnishi, Tsuyoshi)
物質・材料研究機構・国際ナノアーキテクト
ニクス研究拠点・MANA研究者
研究者番号:80345230