Electron transport across complex oxide heterointerfaces

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Summary

The development of electronic and spintronic devices has been spurred by novel materials with new functionalities. In this context, complex oxides are an important addition to the next generation of spintronic devices. In complex oxides, the physical properties can be tuned by altering the various degrees of freedom, namely: spin, charge, and orbital. Fabrication of complex oxide based solid state devices to investigate charge and spin transport is challenging. Such devices are also relevant for the International Technology Roadmap for Semiconductors (ITRS), which has included such materials and their devices in their recent edition.

In this thesis, we have investigated hot electron transport in a strongly correlated oxide and across their heterointerfaces, using a nanoscale technique called ballistic electron emission microscopy (BEEM). An understanding of hot electron transport is fundamental to the operation of several solid state devices namely: hot electron transistor, spin valve transistor or magnetic tunnel transistor. However, until now electron and spin transport in such devices has been investigated using conventional metals and ferromagnets. In our study, we used a doped manganite and its interface with an oxide semiconductor and investigated its charge transport. The basic concepts of electron transport across a metal-semiconductor (M-S) Schottky interface, the commonly used transport models, and a theoretical understanding of hot electron transport are discussed in details in this thesis. For our studies, we first grew epitaxial, stoichiometric thin films of $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) on single crystalline semiconductor, Nb doped $SrTiO_3$, using pulsed laser deposition (PLD) with monolayer precision. Thereafter, an extensive investigation of their physical properties as, structural, electrical and magnetic properties was done. Next, we studied the electrical properties of Nb doped $SrTiO_3$ as well and its heterointerfaces with different metals. We found that the resistivity and mobility are temperature dependent in

the doped semiconductor whereas the carrier concentration is almost temperature invariant.

For the first time, a systematic study of electron transport across heterointerfaces between Nb:$SrTiO_3$ and metals like gold (Au) and copper (Cu), and LSMO (a complex oxide metal) is performed. The role of the dielectric permittivity of Nb:$SrTiO_3$, in electronic transport across heterointerfaces is discussed. Further, a nanoscale technique called ballistic electron emission microscopy (BEEM), is employed to investigate perpendicular transport across such interfaces. The utilization of BEEM in characterizing electron transport and probing local inhomogeneities across such unbiased oxide interfaces is demonstrated. Additionally, the thickness dependent hot electron transport in LSMO, at the nanoscale, is presented. A comprehensive study of hot electron transport in LSMO, using BEEM, on an atomically engineered epitaxial interface is performed to quantify the hot electron attenuation length. Similar studies are extended to pristine LSMO interfaces with Nb:$SrTiO_3$. A comparison of the attenuation length in an engineered and a non-engineered interface is discussed. The thickness dependence of the local Schottky barrier height across epitaxial LSMO/Nb:$SrTiO_3$ interface is also discussed. Finally, some insights into the tunneling spin polarization of LSMO in a magnetic tunnel junction device configuration is presented.

This thesis is a first work that demonstrates the application of Ballistic Electron Emission Microscopy (BEEM) to the study of hot-electron transport in complex oxide heterostructures. Key transport parameters as the hot electron attenuation length and its energy dependence are successfully obtained for LSMO. Such a work can be easily extended to the study of hot electron transport in other oxide materials as ruthenates and multiferroics. An important finding in this thesis is the strong contribution of polaron scattering in addition to the electron-electron scattering to the energy dependence of the attenuation length in such transition metal oxides. From device perspective, there has been much recent interest in devices based on hot-electron transport, such as in photovoltaic effects in multiferroics, or ferroelectric tunneling electroresistance. This approach of using non-equilibrium transport will also be appealing for theorists where it could be used to measure equilibrium self-energy corrections arising from correlations. The unique capability of this technique to map electron transport in buried layers and interfaces is extremely important for designing and understanding transport in oxide electronic devices and this work is a first demonstration in this direction.

Samenvatting

De ontwikkeling van elektronische en spintronische devices wordt gestimuleerd door de ontdekking van nieuwe materialen met nieuwe functionaliteit. In die context vormen complexe oxides een belangrijke bijdrage voor de volgende generatie spintronische devices. In complexe oxides kunnen de fysische eigenschappen veranderd worden door het aanpassen van de verschillende vrijheidsgraden: spin, lading en orbitalen. Fabricage van vaste-stof devices gebaseerd op complexe oxides om lading- en spintransport te bestuderen, is uitdagend. Zulke device structuren worden ook als belangrijk aangemerkt in de International Technology Roadmap for Semiconductors (ITRS) die het gebruik van deze materialen en gerelateerde device structuren hebben toegevoegd aan hun recente editie.

In deze these, hebben we hot electron transport in sterk gecorreleerde oxide materialen en hun hetero-interfaces bestudeerd; gebruikmakend van een nanometerschaal techniek genaamd Ballistische Elektronen Emissie Microscopie (BEEM). Inzicht en begrip van heet elektron transport is van fundamenteel belang voor de werking van vaste stof devices zoals de hot electron transistor, spin valve transistor en magnetische tunnel transistor. Echter, tot dusver is ladings- en spintransport in zulke devices bestudeerd door gebruik te maken van conventionele metalen en ferromagneten. In onze studie gebruiken we gedoteerd manganiet in contact met een oxide halfgeleider en bestuderen we ladingstransport. De basisconcepten van ladingstransport door het metaal-halfgeleider (M-H) Schottky grensvlak, de gebruikelijke transportmodellen, en het theoretisch begrip van heet elektron transport is gedetailleerd beschreven in deze these.

In onze studie hebben we allereerst epitaxiale, stoichiometrische dunne lagen $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) gegroeid op een kristallijne halfgeleider, Nb gedoteerd $SrTiO_3$, door middel van gepulseerde laser depositie (PLD) met monolaag precisie.

Vervolgens is een uitgebreide studie uitgevoerd naar de fysische eigenschappen (zowel structurele, elektrische en magnetische) van dit materiaal. Verder hebben we de elektrische eigenschappen van Nb gedoteerd $SrTiO_3$ en de hetro-interface tussen deze halfgeleider en verschillende metalen bestudeerd. Hieruit blijkt dat het weerstandsvermogen en de mobiliteit temperatuurafhankelijk zijn in de gedoteerde halfgeleider terwijl de ladingsdragerconcentratie bijna temperatuuronafhankelijk is.

Voor het eerst is een systematische studie naar ladingstransport door de hetero-interfaces tussen Nb:$SrTiO_3$ en metalen zoals goud (Au) en koper (Cu), en LSMO (een complexe metaal oxide) uitgevoerd. De rol van de dilektrische permittiviteit van Nb:$SrTiO_3$ in ladingstransport aan deze interfaces is bestudeerd. Verder is BEEM gebruikt om loodrecht ladingstransport aan deze grensvlakken te onderzoeken. Het gebruik van BEEM in het karakteriseren van ladingstransport en lokale oneffenheden aan zulke unbiased oxide grensvlakken is beschreven in deze these. Hierbij is ook de dikteafhankelijkheid van het hete elektron transport in LSMO op lokale nanometer schaal onderzocht. Een uitgebreide studie naar heet elektronen transport in LSMO, met BEEM, door een gemodificeerd epitaxiaal gegroeid grensvlak is uitgevoerd om de attenuatie-lengte van de hete elektronen te kwantificeren. Vergelijkbare studies zijn gedaan aan zuivere LSMO/Nb:$SrTiO_3$ grensvlakken. Een vergelijking tussen de attenuatie-lengte van een gemodificeerd en niet-gemodific eerd grensvlak is gemaakt. De dikteafhankelijkheid van de lokale Schottky barrire hoogte aan een LSMO/Nb:$SrTiO_3$ grensvlak is beschreven. Tenslotte beschrijven we inzichten in de tunnel spin polarisatie van LSMO in een magnetische tunnel junctie configuratie.

Deze these is het eerste verschenen werk dat het gebruik van BEEM om heet elektron transport in complexe oxide heterostructuren te bestuderen, demonstreert. Belangrijke transportparameters van LSMO zoals de hete elektron attenuatie-lengte en de energieafhankelijkheid zijn succesvol verkregen. Dit werk kan verder uitgebouwd worden naar studies van andere complexe oxides zoals ruthenates en multiferroics. Een belangrijke conclusie in deze these is de sterke bijdrage van polaron botsingen , naast electron-electron botsingen, aan de attenuatie-lengte in zulke transitie metaaloxides. Er is recent veel interesse in device structuren gebaseerd op heet elektron transport zoals photovoltaische effecten in multiferroics of ferroelektrische tunneling elektroweerstand. De gebruikte benadering van non-equilibrium transport is ook interessant voor theoretici, waar het gebruikt kan worden om equilibrium self-energie correcties, veroorzaakt door correlaties, te meten. De unieke mogelijkheid om met deze techniek elektronen transport te visualiseren en kwantificeren in verborgen lagen en grensvlakken is zeer belangrijk voor het ontwerpen en begrijpen van transport in elektronische oxide devices, dit werk is een eerste demonstratie in deze richting.

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List of publications

1. "Evidence of spin scattering and collection of hot electrons at different conduction minima in Si",
   S. Parui, **K. G. Rana** and T. Banerjee,
   accepted in *Appl. Phys. Lett.*

2. "Probing hot electron transport across an epitaxial Schottky interface of $SrRuO_3$ /Nb:$SrTiO_3$",
   S. Roy, A. M. Kamerbeek, **K. G. Rana**, S. Parui and T. Banerjee,
   Appl. Phys. Lett. **102**, 192909 (2013).

3. "Probing electron transport across a LSMO/Nb:STO heterointerface at the nanoscale",
   K. G. Rana, S. Parui and T. Banerjee,
   Phys. Rev. B **87**, 085116 (2013).

4. "Hot electron transport in a strongly correlated transition metal oxide",
   K. G. Rana, T. Yajima, S. Parui, A. F. Kemper, T. P. Devereaux, Y. Hikita, H. Y. Hwang and T. Banerjee,
   Sci. Rep. **3**, 1274 (2013).

5. "Comparison of hot-electron transmission in ferromagnetic Ni on epitaxial and polycrystalline Schottky interfaces",
   S. Parui, **K. G. Rana**, L. Bignardi, B. J. van Wees and T. Banerjee,
   Phys. Rev. B **85**, 235416 (2012).

6. "Electrical transport across Au/Nb:$SrTiO_3$ Schottky interface with different Nb doping",
   K. G. Rana, V. Khikhlovskyi, and T. Banerjee,
   Appl. Phys. Lett. **100**, 213502 (2012).

7. “Nanoscale hot electron transport across Cu/n-Si(100) and Cu/n-Si(111) interfaces”,
S. Parui, J. R. R. van der Ploeg, **K. G. Rana** and T. Banerjee,
Physica Status Solidi (Rapid Research Letters) **5**, 388 (2011).

8. “Spin transport in metal and oxide devices at the nanoscale”,
S. Parui, **K. G. Rana** and T. Banerjee,
Electron Devices Meeting (IEDM), 2012 IEEE International, 11.4.1-11.4.4, (2012).

9. “Evolution of the bulk properties, structure, magnetic order, and superconductivity with Ni doping in $CaFe_{2-x}Ni_xAs_2$”,
N. Kumar, S. Chi, Y. Chen, **K. G. Rana**, A. K. Nigam, A. Thamizhavel, W. Ratcliff II, S. K. Dhar, J. W. Lynn,
Phys. Rev. B **80**, 144524 (2009).

10. “Temperature dependence of hot electron attenuation length LSMO/Nb:STO”,
K. G. Rana *et al.*, in preparation.

11. “Thickness dependent electrical transport in LSMO thin films”,
K. G. Rana *et al.*, in preparation.

12. “Electronic transport at the nanoscale across noble metal/Nb:STO interface”,
K. G. Rana *et al.*, in preparation.

Curriculum Vitae

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Education

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