Charge and spin transport across graphene and multifunctional oxide interfaces

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Summary and outlook

Since the invention of transistors in the mid-20th century, we have entered the Information Age. In this Age, the social evolution has been driven by modernized information and communication technology. Such technology advances are governed by three important laws: Moore's law, Kryder's law and Koomey's law. They describe the scaling of the number of transistors, the amount of storage space, and the power consumption density, respectively. However, further downscaling leads to reaching the limits of miniaturization at atomic levels. Spintronics is a potential candidate to substitute electronics for future information technologies, in terms of both data storage and logic computing. Graphene, a two-dimensional material with an atomic thickness, is ideal for the spintronics application due to its superior intrinsic mobility, low spin-orbit coupling and weak hyperfine interaction. Furthermore, when in proximity with multifunctional oxides, graphene either inherit the properties or is susceptible to the environment at the interface between graphene and oxides. This thesis focuses primarily on understanding the spin and charge transport across graphene and multifunctional oxide interfaces, and the potential implications thereof for future electronic devices.

The material systems involved in this thesis, i.e. graphene, $SrTiO_3$ (STO), and $BiFeO_3$ (BFO), are described in **chapter 2**. An introduction is given into the crystal structure and band structure of graphene. Based on this, the electronic transport properties of graphene are discussed. In addition, STO, a universal substrate for complex oxides, is reviewed in terms of phase transition, domain formation, oxygen vacancies, and spin-orbit coupling. Finally, the multifunctional complex oxide BFO is examined in three aspects: structural and ferroelectric properties, magnetic properties, and the coupling between ferroelectric and magnetic orders.

Basic theoretical concepts that play an important role in this thesis are described in **chapter 3**. Starting from an early model to understand spintronics, the two-current model, graphene spintronics is discussed. A local spin valve based on giant magneto-resistance is explained. Additionally, three essential processes in spintronics are described: spin injection, spin transport, and spin detection. At the basis of spin transport characterization in graphene, lay non-local and Hanle measurements. Also, the proximity effect is discussed, introducing additional functionalities in graphene. In the second half of this chapter, spintronics in magnetic insulators is discussed. The basics of magnetic dynamics are described, as well as spin Hall magneto-resistance and spin Seebeck effect are reviewed. These are efficient tools to detect the magnetic order in the magnetic insulator.

Chapter 4 discusses the basic experimental techniques that are involved in this thesis. Fabrication details, including exfoliation, transfer of two-dimensional materials onto desired substrates, and electron beam lithography are described. Also, the details of the measurement techniques are explained.

What makes graphene a promising material in spintronics are the theoretically predicted intrinsic spin relaxation time of up to $1\,\mu s$ along with extremely high charge carrier mobilities. Numerous experimental studies, however, find the spin lifetime in graphene to be several orders of magnitude below that theoretically predicted. Additionally, an analysis of the spin relaxations mechanisms in graphene shows a coexistence of both Elliot-Yaffet (EY) and D'Yakonov-Perel' (DP) mechanisms, with no clear dominance of either. Central to these experimental discrepancies is the role of the local environment, including that of the underlying substrate. In **chapter 5**, we focus on integrating graphene with complex oxides. Namely, we use the electronically rich platform of STO with broken inversion symmetry and study spin transport in graphene in the presence of surface electric fields. We report on the first observation of spin transport in graphene on TiO_2 terminated STO with broken inversion symmetry. A spin relaxation time and length as large as $0.96\pm 0.03\,ns$ and $4.1\pm 0.1\,\mu m$ are found at $290\,K$ in graphene, using non-local spin valve studies. These parameters have a non-monotonous dependence with temperature at low temperatures. This is different from what is observed in other substrates. Additionally, we find that spin transport in graphene on STO is influenced by the cumulative effect of surface electric dipoles, intrinsic spin orbit coupling and temperature induced rippling of the graphene interface. The gate dependence of the spin relaxation parameters at 4 K is attributed to the modulation of the strength of the surface dipoles in STO, while an analysis of the spin relaxation mechanism shows the coexistence of both EY and DP scattering processes. The results in this chapter opens up new opportunities to study proximity induced functionalities at such interfaces, useful for future spintronics and optoelectronics applications.

Heterointerfaces coupling complex oxides exhibit coexisting functional properties such as magnetism, superconductivity and ferroelectricity, often absent in their individual constituent. STO, a canonical band insulator is an active constituent of such heterointerfaces. Temperature, strain or mechanical stress induced ferroelastic transition leads to the formation of narrow domains and domain walls in STO. Such ferroelastic domain walls have been studied using imaging or transport techniques, and often the findings are influenced by the choice and interaction of the electrodes with STO. The unique physical and chemical properties in graphene, specifically the van der Waals bonding nature, prevents unwanted electrode-substrate (STO) interaction, facilitating the identification of the exact mechanism responsible for the anti-hysteresis in the square resistance in graphene. In **chapter 6**, we use a monolayer graphene flake as a unique platform to unveil the movement of oxygen vacancies and ferroelastic domain walls near the STO surface, by studying the temperature and gate bias dependence of charge transport in graphene. By sweeping the back gate voltage, we observe anti-hysteresis in graphene typically observed in conventional ferroelectric oxides. Interestingly, we find features in the anti-hysteresis that are related to the movement of domain walls and of oxygen vacancies in STO with an estimated energy barrier of 15 meV. We ascertain this by analysing the time dependence of the graphene square resistance at different temperatures and gate bias. Density functional calculations estimate the surface polarization and formation energies of layer-dependent oxygen vacancies in STO and energy barriers for the diffusion of oxygen vacancy towards the surface of STO and charge transfer at the interface between graphene and STO. This corroborates quantitatively with the activation energies determined from the temperature dependence of the graphene square resistance. Introduction of a hexagonal boron nitride (hBN) layer, of varying thickness, between graphene and STO leads to a gradual disappearance of the observed features, implying the influence of the domain walls onto the potential landscape in graphene. Our approach can be extended to the study of the dynamics of electronic and ionic charge transport and their retention characteristics, using 2D materials onto oxide substrates, paving the way for electric field control of memory functionalities in electronic devices.

Besides STO, another complex oxides with rich intriguing properties is a room temperature multiferroic material, BFO. It has large ferroelectric polarization and a G-type antiferromagnetic (AFM) order. In **chapter 7**, we use the spin Hall magnetoresistance (SMR) and spin Seebeck effect (SSE) for probing the magnetic ordering in BFO. We studied BFO in two different strain states, and thus with different antiferrodistortive and ferroelectric distortions. We observe positive SMR for both samples, but surprisingly, with different temperature dependence. For BFO//STO, the positive SMR reveals the weak ferromagnetism (wFM) in R-like phase BFO, where the antiferrodistortive rotation is large. The temperature dependence of SMR in BFO//STO suggests that the wFM decreases with increasing temperature, which is consistent with DFT calculations. Interestingly, an enhanced signal of SMR at low temperatures in BFO//STO indicates the existence of a spin cycloid at such temperatures. As for BFO//LAO, the wFM is suppressed due to a negligible antiferrodistortive rotation of oxygen octahedra. However, there is a correlation of the spin fluctuations near Néel temperature, leading to a non-zero SMR signal. Moreover, the Néel temperature T_N is around 360 K for BFO//LAO, compared to 675 K for BFO//STO. Above T_N, the BFO//LAO is paramagnetic, while below T_N, BFO//LAO becomes more antiferromagnetic with decreasing temperature, leading to a decreasing SMR amplitude. Using the SSE as a probe, the bulk antiferromagnetic magnons are detected at low temperatures in both samples, whereas the SSE signal in BFO//STO has contributions of both AFM magnons and wFM magnons.

When graphene is in proximity with an antiferromagnetic multiferroic BFO, it opens further possibilities in advancing graphene-based spintronics. In **chapter 8**, we report on proximity effect in graphene and BFO heterostructure by studying its magneto-transport. We attribute the linearity in graphene magnetoresistance at a high magnetic field to significant inhomogeneity in the charge-carrier densities and mobilities of graphene due to the local gating effect from BFO domains. We found further evidence of the inhomogeneity by analyzing the weak localization. It reveals a difference in the phase-coherence time along the graphene channel, which is an indicator of different domain configurations in BFO. In the end, spin relaxation time induced by the local magnetic moments is extracted from the temperature-dependent phase coherence time and found to be 1.2 ps, quantitatively illustrating the strong influence of BFO local magnetic moment on spin transport in graphene. This finding opens an opportunity for realizing spin logic devices by electric field control.

Outlook

This thesis has attempted to explore graphene and complex oxides for a new information technology beyond CMOS. We integrated graphene with complex oxides such as STO and BFO and realized the control of its transport properties. The control of the charge and spin transport in graphene can be exploited in electronic and spintronic applications, respectively. Furthermore, the ability to electrically read out the magnetic state in BFO paves the way for the realization of a new type of logic device: magneto-electric spin-orbit (MESO) logic device. This device requires solely an attojoule-level switching energy and a high density of logic elements (a factor of 5 higher than advanced CMOS devices) can be realized using MESO as a basic element.

Specifically the tunability of the spin transport parameters in graphene using STO as a back gate is meaningful for spin logic devices. In this preliminary stage, the tunability is rather limited. In the following work in graphene on BFO, we found a strong influence of BFO on the spin relaxation time of graphene. Manipulation of the ferroelectric domains in BFO might further tune the spin transport in graphene, which has not been explored in this thesis. Thus, one possible way to improve the tunability of spin transport in graphene is to employ the ferro-electricity in BFO. Besides a perspective for applications, by exploring the whole parameter space in the system of graphene on BFO, we might be able to explore quantum mechanical phenomena such as the quantum anomalous Hall effect.

The anti-hysteresis observed in the graphene-STO system can be applied for neuromorphic computing. For such an application, (anti-)hysteresis results in synaptic plasticity, which can be further investigated. In addition to the gating effect, the charge transport in graphene on STO can also be influenced by light, on which we have some preliminary data. Further study is required and can be valuable as application in optoelectronics.

The ability to read out magnetic states in BFO using SMR and SSE is an important process for magneto-electric spin-orbit logic, which has been accomplished in this thesis. Besides, we have some preliminary results on magnon transport in the non-local magnon transport set-up. Here, multiple future research directions can be promising. One is to explore the magneto-electric properties in BFO and realize the control of the SMR readout in BFO by an electric field. Another direction that is also intriguing is the influence of spin cycloid in the efficiency of magnon transport in BFO and its electric field modulation. To summarize, our findings offer a great toolset for both future fundamental research, as well as direct application in logic devices.