MBE GROWTH AND CHARACTERIZATION OF GRAPHENE ON WELL-DEFINED COBALT OXIDE SURFACES: GRAPHENE SPINTRONICS

WITHOUT SPIN INJECTION

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Dissertation Prepared for the Degree of

DOCTOR OF PHILOSOPHY

UNIVERSITY OF NORTH TEXAS

August 2017

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Olanipekun, Opeyemi B. *MBE Growth and Characterization of Graphene on Well-Defined Cobalt Oxide Surfaces: Graphene Spintronics without Spin Injection.* Doctor of Philosophy (Chemistry), August 2017, 88 pp., 3 tables, 49 figures, chapter references.

The direct growth of graphene by scalable methods on magnetic insulators is important for industrial development of graphene-based spintronic devices, and a route towards substrate-induced spin polarization in graphene without spin injection. X-ray photoelectron spectroscopy (XPS), low energy electron diffraction LEED, electron energy loss spectroscopy (EELS) and Auger electron spectroscopy (AES) demonstrate the growth of Co₃O₄(111) and CoO(111) to thicknesses greater than 100 Å on Ru(0001) surfaces, by molecular beam epitaxy (MBE). The results obtained show that the formation of the different cobalt oxide phases is O₂ partial pressure dependent under same temperature and vacuum conditions and that the films are stoichiometric. Electrical I-V measurement of the Co₃O₄(111) show characteristic hysteresis indicative of resistive switching and thus suitable for advanced device applications. In addition, the growth of Co₀.₅Fe₀.₅O(111) was also achieved by MBE and these films were observed to be OH-stabilized. C MBE yielded azimuthally oriented few layer graphene on the OH-terminated CoO(111), Co₀.₅Fe₀.₅O(111) and Co₃O₄(111). AES confirms the growth of (111)-ordered sp² C layers. EELS data demonstrate significant graphene-to-oxide charge transfer with Raman spectroscopy showing the formation of a graphene-oxide buffer layer, in excellent agreement with previous theoretical predictions. XPS data show the formation of C-O covalent bonding between the oxide layer and the first monolayer (ML) of C. LEED data reveal that the graphene overlayers on all substrates exhibit C₃V. The reduction of graphene symmetry to C₃V – correlated with C-O bond formation – enables spin-orbit coupling in graphene. Consequences may include a significant band gap and room temperature spin Hall effect – important for
spintronic device applications. The results suggest a general pattern of graphene/graphene oxide growth and symmetry lowering for graphene formation on the (111) surfaces of rocksalt-structured oxides.
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ACKNOWLEDGEMENTS

I would like to thank God for the gift of life and seeing me through this program despite all challenges. I would like to express my appreciation and gratitude to Dr. Jeffry Kelber for his support and mentoring during my program, and his constructive corrections have really helped me in actualizing my dreams. I also thank the current and past Kelber group members who have helped my understanding of vacuum technology and surface science and those who have helped during my research. Also, I would like to thank the members of my committee for accepting to serve on my dissertation committee and taking out time to review my dissertation.

I would like to appreciate our collaborators who contributed to this work, Dr. Bird’s group at the University of Buffalo, New York, Dr. Dowben’s group at the University of Nebraska, Lincoln, Dr. Goddard III’s group at the California institute of technology and Dr. Priyanka. The financial support from the National science foundation (ECCS-1508991) and C-spin, a Semiconductor Research Corporation program (Task IDs 2381.001 and 2381.006) are greatly appreciated.

I would like to thank my mum for giving me good morals and ensuring my education is of utmost priority to her despite my father’s demise when I was 6 years old and for her love and support. Also, I want to appreciate my siblings for their love and guidance. I would like to say thanks to my friends who have supported me in this journey and also Pastor (Dr.) Kola Sonaike and Pastor (Dr.) Gbolahan Osho who have made my dreams a reality despite all odds. Lastly, I would like to appreciate my loving wife, Oluwashola Olanipekun who supported me and waited with a lot of patience throughout my program.
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CHAPTER 1
INTRODUCTION

1.1 Motivation

The continued downscaling of complementary metal-oxide-semiconductor (CMOS) dimensions, with improvements in technology, is approaching practical and fundamental limits, hence the need for post-CMOS technology to develop new and non-volatile devices which involve electron spin rather than its charge as potential solutions. This aspect of electronics which utilizes the spin of electrons to carry information is called spintronics. This offers opportunities of developing new and novel devices for logic and memory applications, combining the conventional microelectronics with spin-dependent effects arising from the interaction between the spin of the electron and the magnetic properties of the material [1–3]. Combining the spin degree of freedom with a conventional charge-based semiconductor, or using the spin degree of freedom alone has the potential to significantly enhance performance and functionality to electronics devices [1].

Since the discovery of graphene [4], there has been a great interest in the study of graphene spintronics due to its exceptional properties such as long spin diffusion length (order of 100μm), long spin life times, high electron mobility and the feasibility to control its spin rotation by electric field [5–9]. It is also of interest due to predicted spin filtering which allows for preferential tunneling transmission of one spin over the other [10,11]. Graphene possesses a long spin diffusion length as a result of small spin-orbit coupling and negligible hyperfine interaction [12,13]. Advantages of using graphene as a spin carrier for numerous spintronic applications include non-volatility (ability to retain its memory and state when power is lost), low power consumption and increased processing speed [1,14–16].
The six major roadblocks in developing non-volatile graphene spin-based devices are (a) growing graphene on an insulating substrate; (b) injecting spins in graphene from a switchable magnetic electrode; (c) the slow switching speed of ferromagnetism; (d) the dominant edge scattering as the graphene conducting channel drops below 50 nm; (e) the lack of a viable and controllable band gap; and (f) the very low magneto-resistance values at room temperature, in graphene. Most reports of graphene based spintronic device fabrication involved the peeling off of graphene from HOPG or growth on a catalytic metallic substrate and then physically transferred on an insulating or dielectric substrate [6,17,18]. This method is not industrially practical and scalable. A way to circumvent this problem is to grow graphene directly onto the required dielectric substrate.

One of the major problems encountered in graphene spintronics is inefficient injection of highly spin-polarized electron into graphene from a ferromagnetic substrate and this is due to the conductivity mismatch [19] between graphene and the ferromagnetic metal. This results in a lot of spins being rejected and a low degree of spin polarization [9,19,20]. Spin injection even with tunneling barriers such as MgO has proved inefficient [9,21–26]. An alternative approach is spintronics without spin injection by substrate induced spin polarization when graphene is in proximity to a magnetic material [17,18,27–29]. This involves spin polarizing graphene conduction electrons by an adjacent magnetic material due to the exchange interaction between the spins in the graphene and the magnetic material. Therefore, solving both problems hindering the development of non-volatile graphene spintronic device involves the direct growth of azimuthally oriented few layer graphene on magnetic oxide substrates. Recent experiments [29] have demonstrated the layer-by-layer growth of graphene on 10 Å thick antiferromagnetic \( \text{Co}_2\text{O}_4(111)/\text{Co}(0001) \), with evidence strongly suggesting oxide-induced spin polarization of the
graphene to $> 400$ K, due to interactions with the boundary layer magnetization of the oxide substrate [28]. This involves an exchange interaction between the top-most layer of electrons in the magnetic oxide and the layer of electrons, in the graphene, leading to an overall spin polarization of the graphene conduction electrons.

Theoretical studies have shown that graphene conduction electrons can be polarized through proximity effect when deposited on a magnetic oxide [27]. Very recent work by the Kelber group, in collaboration with the Goddard group [30], predicts that graphene epitaxy on Co$_3$O$_4$(111) is mediated by the formation of an interfacial graphene oxide layer featuring graphene to magnetic oxide charge transfer via C-O bond formation. This work predicts that such a process should also occur on other p-type magnetic oxides, including CoO(111) and spinels, such as CoFe$_2$O$_4$ (which is ferrimagnetic with a $T_c \sim 790$ K).

The fabrication of graphene spin-based devices by direct growth, using industrial scalable methods rather than by physical transfer of graphene, is of fundamental interest and technological importance. Most of the work reported in the literature has used physical transfer of a single layer of HOPG graphite, or a layer of graphene grown on Cu, to a substrate such as SiO$_2$/Si for subsequent electronic measurements. The process leaves defects and contamination on the films and at the film/substrate interface, impacting graphene properties. Perhaps more importantly, however, this approach has obvious limitations regarding the large scale production of devices [31,32].

This work is part of a collaborative effort in fabricating graphene based spintronic device. The focus of this research is to grow a well-defined Co$_3$O$_4$(111) and CoO(111) interfaces on Ru(0001) and to explore the direct growth and characterization of epitaxial graphene films on these surfaces by scalable and reproducible methods and to verify the predictions of the model of
C-O covalent bond formation. Ru has been chosen as the base metal because of its compatibility with current CMOS and 2D materials application [33,34].

1.2 CoO(111) and Co$_3$O$_4$(111)

Transition metal magnetic oxides are an important group of oxides which find use in catalysis, electronic and magnetic devices [35] and in magneto-electric devices [36]. Cobalt oxides are a class of these transition metal magnetic oxides that find widespread use as a result of their surface redox reactivity properties [37]. Cobalt oxides find wide use as lithium ion battery electrodes, field emission material, magnetic materials [38] and also serve as dielectric support for the growth of 2D materials such as graphene [29].

CoO(111) has a rock salt structure with the Co in the +2 oxidation state occupying the octahedral sites and has a closed packed O$^{2-}$ arrangement [39]. It has a symmetry space group of Fm3m at 300K[37]. CoO displays antiferromagnetic ordering below 291 K and is an insulator with a band gap of ~4-6eV [39]. Co$_3$O$_4$(111), on the other hand is a spinel magnetic oxide where the Co$^{3+}$ is octahedrally coordinated and Co$^{2+}$ is tetrahedrally coordinated and is thermodynamically stable at ambient room temperature and O$_2$ partial pressure [37]. It has a space group of fd3m at room temperature [37]. It is antiferromagnetic below ~ 40 K as a result of the antiferromagnetic ordering of spins of the Co$^{2+}$ in the tetrahedral sites [40,41]. It is a p-type magnetic oxide with a band gap of ~2.2 eV [42]. Cobalt oxide films are of interest in a variety of spintronic applications [43] and in spin valve [44]. With respect to spintronic applications, recent demonstration of graphene deposition on Co$_3$O$_4$(111)/Co(0001) with resulting magnetic hysteresis to > 400 K suggest that Co$_3$O$_4$(111) and possibly other magnetic oxides with p-type character may serve as promising substrates to induce graphene spin polarization as an alternative to spin injection [27–29].
Therefore, Co$_3$O$_4$(111) and CoO(111) grown on Ru(0001) will be explored as magnetic oxide substrates due to previous results of magnetic hysteresis obtained at and above room temperature [28] and also the fact that CoO(111) has an antiferromagnetic ordering greater than Co$_3$O$_4$(111), we should expect to have magnetic hysteresis above room temperature. However, the (111) surfaces of polar oxides with the rock salt structure such as CoO(111) are unstable and prone to reconstruction due to the high surface potential and uncompensated surface charge [45–47]. This surface polarization can however, be reduced by surface hydroxylation thereby stabilizing the (111) surface [48–50]. This work is focused on the growth of these oxides and subsequent graphene growth to study the formation of C-O formation as an interfacial layer for further graphene growth and to study the charge transfer from C to the oxide leading to the stability of the graphene on the magnetic oxides. The films made are characterized by AES.

\textbf{Figure 1.1.} A ball and stick model of (a) CoO(111); (b) Co$_3$O$_4$ (111) drawn by Vesta software.
EELS, XPS and LEED. Since the phases of cobalt oxides are O\textsubscript{2} pressure dependent, the O\textsubscript{2} pressure required to form CoO(111) in this work was 7.5\times10\textsuperscript{-7} Torr while a higher pressure of 1\times10\textsuperscript{-4} Torr was used to produce Co\textsubscript{3}O\textsubscript{4}(111).

1.3 Graphene

Graphene is a 2D layer of sp\textsuperscript{2} bonded C and which is one-atom thick and is a zero band gap semiconductor. There has been lot of interest in the study of graphene in spintronic majorly due to its excellent electrical, thermal, optical, mechanical properties and room temperature hall effect [51–55]. Also, is the prediction of spin induced polarization of the graphene layer when deposited on a magnetic material [27]. Reports show that the thermal conductivity of graphene is \sim5000 Wm\textsuperscript{-1}k\textsuperscript{-1}, Young’s modulus of \sim1100 GPa, mobility of charge carriers of 200,000 cm\textsuperscript{2}v\textsuperscript{-1}s\textsuperscript{-1} for unsuspended graphene and very long electron spin diffusion length of the order of 100 \mu m [7,56] and has been reported to be sensitive to the proximity of the other materials such as ferromagnets and magnetic oxides [27]. Due to this excellent properties, graphene is a better electron transport material than other carbon materials for spintronics application [57]. Other allotropic forms of carbon are the 3D forms (graphite and diamond), 0D (fullerenes) and 1D forms (carbon nanotubes) [58–60].

As graphene is an sp\textsuperscript{2} carbon, the hybridization between the s-orbital and the two p-orbitals leads to a trigonal planar geometry. The separation of the C atoms is 1.42 Å and they have \sigma -bond between them [61].

The charge carriers in graphene are described by the Dirac-like equation shown in equation 1.1 [62]

$$\hat{H}_0 = -i\hbar |v_F| \sigma \nabla$$

Equation 1.1

Where $\sigma = (\sigma_x, \sigma_y)$ are the Pauli matrices and $v_F$ is the Fermi velocity ($\sim 10^6$ ms\textsuperscript{-1})
This equation is as a result of the graphene’s crystal structure shown in figure 1.2a consisting of 2 equivalent C sub-lattices. Figure 1.2b shows the formation of 2 energy bands with the intersection near the edges of the Brillouin zone yielding the conical energy spectrum near the Dirac points k and k’[62]. As a result of these, graphene electrons travel as massless quasiparticles (Dirac fermions) [63]. This properties makes graphene a good candidate for spin carrier in a spin-based device with high processing speed.

![Figure 1.2.](image)

**Figure 1.2.** (a) The structure of graphene and (b) the structure of graphene [62]

1.4 Ru(0001) Surface

Ru(0001) is a transition non-magnetic metal with a hexagonal closed packed crystal surface and a lattice constant of a=2.71 Å and a high melting of 2538 K [64] and is stable thermally and chemically. It is a material that is compatible with current CMOS technology [34] and can allow the growth of 2D materials such as graphene [33,65,66]. The close lattice constant of Ru to the O-O sub-lattice of 2.85Å in cobalt oxides and the ability to form conformal and epitaxial Ru(0001) on Al2O3(0001) makes it an ideal candidate as a metal base layer [67].

For this work, Ru(0001) films were grown on Al2O3(0001) by DC magnetron sputter deposition on a commercially available Al2O3 in a separate chamber and then transferred through air to another chamber for treatment and for the growth of cobalt oxides, graphene and analysis.
1.5 Spin Induced Polarization of Graphene in Proximity to Magnetic Materials

Spintronics involves the injection, manipulation and detection of spins in electronic systems. Injection of spins from a magnetic material directly into a semiconductor such as graphene is difficult to achieve due to conductivity mismatch between the semiconductor and the magnetic material used as contacts [20]. However, to overcome this mismatch, the use of a tunneling barrier is used to create a sufficiently high resistance between the interface of the semiconductor and the magnetic material as shown in figure 1.3 [26]. This method only measures a magneto-resistance (MR) value of ~9.4% at ~2 K but higher magneto-resistance values are needed for high ON/OFF ratio devices [7].

The magneto-resistance (MR) is the resistance change induced when switching the spin polarization in the graphene channel to that of the drain:

\[ MR = \frac{(R_{\text{AP}} - R_p)}{(R_p)} = \frac{(G_p - G_{\text{AP}})}{G_{\text{AP}}} \]  

Equation 1.2

where \( R_p \) and \( R_{\text{AP}} \) are resistances and \( G_p \) and \( G_{\text{AP}} \) are the conductances for the source and the drain in parallel and antiparallel configuration [19].

In order to obtain higher MR values, spin induced polarization and transport has been predicted in graphene when in proximity to a magnetic insulator. This is thought to be due to the

![Figure 1.3. The Conventional spin-FET exploring spin injection.](image-url)
exchange splitting induced in the graphene [27]. A high MR value of up 200% has been reported for graphene on ferromagnetic material and its dependent on the applied bias as shown in figure 1.4 [68].

**Figure 1.4.** (a) The schematic model of a spin polarization (b) Bias dependence of magneto-resistances [68].

Magneto-resistance is related to the spin polarization of conduction electrons. The spin polarization is defined as:

\[ P_N = \frac{N_{\uparrow} - N_{\downarrow}}{N_{\uparrow} + N_{\downarrow}} \]  

Equation 1.3

**Figure 1.5.** The spin-FET based on the induced polarization of the graphene conduction electrons.

Figure 1.5 shows a typical graphene spin-FET fabricated in this work which is based on the polarization of the graphene layer as a result of the electron interaction of the graphene layer with the magnetic oxide substrate.
Graphene might possess some defects that scatters electrons and thereby reducing the transport length of its electrons [63]. However, for the type of spin based device fabricated in this work, defects shouldn’t affect the performance of the device as the graphene conduction electrons should be polarized evenly as shown in figure 1.6b as opposed to conventional spin-based devices shown in figure 1.6a.

![Figure 1.6](image)

**Figure 1.6.** The polarization (P) of graphene conduction electrons as a function of channel length (X) in (a) a conventional spin-FET exploring spin injection and (b) a proposed or predicted spin-FET exploring spin-induced polarization.

But these defects can indeed be reduced by using the appropriate deposition techniques and depositing graphene on an ordered surface.

A general and fairly typical method reported in the literature for the deposition of graphene is the transfer of flakes by the scotch tape method which involves placing the HOPG on an adhesive tape and peeling the flakes off repeatedly until the thinnest flakes are obtained and then transferred to a suitable substrate. This method has been reported to produce high quality graphene [4,54]. Another method is to grow graphene on a metal surface by chemical vapor deposition and then physically transfer the graphene to a suitable substrate for further studies as shown in figure 1.7 [16,69]. Both of these methods are time consuming and are delicate. They are not scalable, cause azimuthal misalignment of the film and the film is also prone to contamination.
Leutenantsmeyer et al. [18] reported on the direct measurement of exchange interaction at room temperature when graphene was exfoliated on Yttrium-iron-garnet. They observed the presence of an exchange field with a strength of the order of 0.2 T which is an evidence of induced magnetism. They further demonstrated that this induced magnetism can be modulated by changing the direction of the applied field [18]. This experiment used the peel off method to obtain graphene from an HOPG. A recent study also demonstrated the successful growth of graphene on a half metallic manganite La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) with a measure of a sizable spin polarization in parallel to the spin polarization direction of LSMO [17]. However, this process involves the CVD of single layer graphene sheet on Cu and then physically transferred onto the LSMO thin film using PMMA. These methods are however limited to a single layer of graphene and are not scalable [17].

The direct growth of epitaxial graphene on insulating magnetic oxide substrate is the best route towards making graphene-based spintronic devices. To achieve the direct growth of graphene, MBE would be explored the technique is scalable and compatible with existing CMOS
processing technologies. The MBE process involves evaporating pure C rods (99.999% purity) by a heated filament onto a magnetic oxide substrate.

1.6 Theoretical Predictions of Graphene Nucleation on p-Type vs n-Type Magnetic Oxides

Work done on graphene growth on BN showed that the graphene layers are in registry with the BN substrate with no indication of any charger transfer from the graphene to the BN and vice versa [70]. This is indeed expected as the lattice constant of graphene of 2.46 Å [71,72] closely matched that of BN of 2.5 Å [73] and the type of interaction between this layers is Van der Waals epitaxy as both graphene and BN are chemically inert. However, the MBE growth of graphene was achieved at temperature >800 K on an incommensurate Co$_3$O$_4$(111)/Co(0001) surface with O-O sub-lattice of 2.85 Å and with significant charge transfer from the graphene to the oxide layer [29,67]. This wouldn’t have been expected due to ~14% lattice mismatch between graphene and Co$_3$O$_4$ and a close work function of 4.6eV for graphene [74] and 4.5eV for Co$_3$O$_4$ [75]. Unfortunately the same growth method at 700K does yielded only disordered graphite but not graphene on Cr$_2$O$_3$/Co(0001) with similar O-O sub-lattice constant and work function as Co$_3$O$_4$ [76,77] and annealing to 800K desorbs the C[30]. This shows that lattice matching is probably not the driving force for graphene nucleation on an incommensurate substrate.

In UHV, Co$_3$O$_4$(111) is p-type while Cr$_2$O$_3$ is n-type [42,78,79]. Recent DFT calculations and experiment by Beatty et. al[30] showed that graphene can nucleate on p-type Co$_3$O$_4$(111) as a result of charge transfer as evidenced experimentally in reference [29] while such charge transfer is not seen in graphene deposited on Cr$_2$O$_3$ [30]. Hence, graphene does not seem to nucleate on n-type Cr$_2$O$_3$. It was proposed that graphene is able to nucleate on p-type Co$_3$O$_4$(111) by forming a C-O covalent bond with the first layer of graphene making a rumpled or distorted
graphene layer with an average distance of ~2.67 Å between the first graphene layer and the oxide surface while subsequent graphene layers are expected to have the normal interlayer distance of ~3.43 Å as shown in figure 1.8 [30]. The calculation also predicted ~25% of the C atoms in the first layer to be responsible for the formation of the C-O bond and that ~0.08 electrons/carbon atom are transferred from the first graphene layer to the oxide substrate. This predictions gives us a range of p-type magnetic oxide insulators to explore to make spintronic devices.

Figure 1.8. The nucleation of graphene on Co$_3$O$_4$ (111) predicted from DFT calculation: (a) Top view of 1ML of graphene on Co$_3$O$_4$ (111) (b) Top view of 2ML of graphene on Co$_3$O$_4$ (111) (c) Side view of 1ML of graphene on Co$_3$O$_4$ (111); (d) Side view of 2ML of graphene on Co$_3$O$_4$ (111). Co (blue), O (red), second layer C (yellow), first layer C (silver); C on Co site (dark blue); and C on O site (orange) [30].
1.7 References


[37] S.C. Petitto, E.M. Marsh, G.A. Carson, M.A. Langell, Cobalt oxide surface chemistry: The interaction of CoO(1 0 0), Co3O4(1 1 0) and Co3O4(1 1 1) with oxygen and water, J.


2.1 Ultra High Vacuum

This study involves deposition and characterization under ultra-high vacuum (UHV). UHV is required to avoid undesired reaction of background gases with the adsorbed atoms or substrate so as to maintain a contamination-free substrate during the period of experiment. This is the most important reason very good vacuum is needed for spectroscopic studies and surface science. Assuming a trapping probability or sticking coefficient of 1 for a reactive gas striking a reactive surface in a background pressure of $10^{-6}$ Torr, an adsorption of a monolayer (ML) of the reactive gas molecules (contaminant) can be formed on the substrate in 1 sec at room temperature. Therefore, keeping reactive surfaces atomically clean (e.g. metals, many oxides etc.) over the several hours to perform depositions and acquire data requires the use of UHV (pressure $< 1x10^{-9}$ Torr) [1,2]. UHV is also required to increase the mean free path of particles (such as electrons, ions and atoms) as they travel from the probes (e.g Auger electron gun) to the sample and from the sample towards the analyzer with no interference from gas phase scattering [1].

The UHV system used in this work is an MBE/surface analysis system (figure 2.1) which consists of the sample introduction (load lock), MBE deposition and surface analysis chambers which are separated by manual gate valves and connected by a magnetically coupled feedthrough for sample transfer. The intro chamber/load lock is pumped down by turbo pumps to a base pressure of $4x10^{-9}$ Torr. The MBE deposition chamber is pumped by a turbo-molecular pump achieving a base pressure of $2 \times 10^{-10}$ Torr and it’s equipped with a multisource electron beam evaporator, a sample heating system (300 K -1100 K) and a type K thermocouple mounted in
vicinity to the sample. The MBE system is capable of co-deposition of metals and carbon from rod sources at a controlled flux rate. The main/analysis chamber is pumped by a combination of ion pump/titanium sublimation pump (TSP) and yields pressure at the $10^{-11}$ Torr regime. The UHV chamber is also pumped by a turbo-molecular pump for roughing under high gas loads, such as during Ar$^+$ ion sputtering and annealing in oxygen.

![Figure 2.1. The schematic of UHV system used here](image)

After a cleaning process with repeated cycles of Ar$^+$ ion sputtering and annealing, the substrate sample to 1000 K in the UHV chamber, the MBE of the magnetic oxide films were carried out on the sample in the deposition chamber. The sample is introduced into the deposition chamber and placed on a uni-directional sample manipulator. The manipulator enables resistive heating and the sample temperature can be monitored using a K-type thermocouple spot welded to the center of the sample stage. The ion/titanium sublimation pump
surface analysis chamber (base pressure $7 \times 10^{-11}$ Torr) included a commercially available double pass cylindrical mirror analyzer with co-axial electron gun for AES and EELS measurements, and an unmonochromatized dual anode x-ray source operated at 15 keV and 300 W, for XPS. The system was also equipped with a reverse-view video LEED system, and with an ion gun for sample cleaning. AES spectra were acquired in integral mode and differentiated by computer. For AES, XPS and EELS, the analyzer was operated in fixed analyzer transmission mode. The chamber has additional variable leak valves that can be used to dose/leak oxygen and other gases to modulate the required chemistry. Pressure in both chambers was monitored by nude ion gauges calibrated to N$_2$.

2.2 Deposition Techniques

2.2.1 Magnetron Sputter Physical Vapor Deposition

In sputtering, energetic ions such as Ar$^+$ from the plasma are accelerated toward a cathode (the target) and bombard the target. Target atoms are ejected and then impinge on the substrate, the anode. In magnetron sputter physical vapor deposition, there is a perpendicular electric field to the target surface and a permanent magnet or electromagnet which create lines of flux perpendicular to this electric field but parallel to the target surface [2]. The presence of the strong magnetic field is to trap free electrons in the magnetic field near the target surface resulting in the concentration and intensification of the plasma above the target. Factors that determines the crystallinity and smoothness or quality of the film includes the deposition temperature, Ar gas pressure, chamber background pressure, plasma power, target-sample distance [3,4]. The schematic of a magnetron sputter deposition process is shown in figure 2.2.

Magnetron DC sputter deposition was used to deposit thick Ru(0001) films onto Al$_2$O$_3$(0001) surfaces in a separate chamber built for growing metal films. This chamber is
pumped by a combination of mechanical and turbo pump. The base pressure of this system is 3x10^{-8} Torr

![Diagram of magnetron sputter deposition process](image)

**Figure 2.2.** The schematic of magnetron sputter deposition process

and it is equipped with an ion gauge and baratron gauge to measure low and high pressure respectively. The sample made here is then transferred via air to a separate MBE/surface analysis chamber.

The Ru(0001) thin film growth was achieved at a plasma power of 15W and 3.5 mTorr at ~700 K producing films of room mean square roughness value (RMS) of less than 1 nm. The estimated thickness was measured by our collaborator, Dr. Jon Bird’s group using X-ray reflectivity (XRR).

2.2.2 Molecular Beam Epitaxy (MBE)

The MBE method involves the growth of epitaxial films by heating the solid source (such as Co rod) by electron bombardment of the source tip in an effusion cell with the filament until the atoms at the target tip sublime, and adsorb on the substrate surface. Ultrahigh vacuum of ~3x10^{-10} Torr is required to avoid undesired reaction of background gases with the adsorbed
atoms or substrate. MBE has been chosen for this study because it presents more advantages than other growth methods such as chemical vapor deposition (CVD) and physical transfer (scotch tape method).

It is a comparatively low temperature process hence minimizes auto-doping and produces ordered and epitaxial films [5]. In MBE, growth rate is precisely controlled hence can grow multi-layers and achieve layer-by-layer growth[6]. MBE is also an industrially compactible process unlike physical transfer which is less efficient for large scale production. MBE has been reported to study the growth of Co$_3$O$_4$ on Ir[7] and Al$_2$O$_3$[8] and also the growth of graphene [6]. The schematics of the MBE process is shown in figure 2.3. For this work, MBE will be used to study the growth of Co$_3$O$_4$, CoO, Co$_{0.5}$Fe$_{0.5}$O and graphene.
2.3 Characterization Methods

2.3.1 X-Ray Photoelectron Spectroscopy (XPS)

XPS is a surface characterization technique used to determine the elemental composition of a sample and to determine the chemical states of the different species of the top 100Å of the sample. The XPS system includes an ultra-high vacuum chamber (10^{-11} Torr), X-ray source, detector and an analyzer. The basic principle involves illumination of a sample by x-rays from either a MgKα (1253.6eV) or AlKα (1486.6eV) resulting in the emission of a core photoelectron into the vacuum with kinetic energy given by equation 2.1 with a resulting hole left as shown in figure 2.4.

![Figure 2.4. The schematic of XPS process [1].](image)

\[ \text{K.E} = h\nu - \text{B.E} - \Phi \]

Equation 2.1

Where K.E is the kinetic energy of the emitted photoelectrons

\( h\nu \) is the energy of the incident x-ray

\( \text{B.E} \) is the binding energy of the ejected electrons

\( \Phi \) is the spectrometer work function

Core electrons from specific atomic orbitals of each element have characteristic binding energy associated with them, therefore the presence of peaks at specific binding energies correspond to the presence of specific species. However, a shift in the respective B.E peaks provide
information on the chemical states of the species such as oxidation states and chemical bonding environments. The intensity of these peaks are related to the concentration of each element in the sample. XPS has the advantage of differentiating between species with different oxidation states and chemical bonding environments. XPS has the ability to determine the thickness of the overlayer film by measuring the attenuation of the substrate intensity by the overlayer. For a substrate, B with an overlayer A of thickness \( t \) shown in figure 2.5.

![Figure 2.5. A two layer system for overlayer thickness calculation](image)

\[
I_A = I^0_A (1 - e^{-\lambda_{A,A} \cos \theta}) \quad \text{Equation 2.2}
\]

\[
I_B = I^0_B (e^{-\lambda_{B,A} \cos \theta}) \quad \text{Equation 2.3}
\]

\( I_A \) and \( I_B \) are the overlayer and substrate intensities respectively.

\( I^0_A \) and \( I^0_B \) are the atomic sensitivity factors.

\( t \) is the overlayer thickness in Å.

\( \lambda_{A,A} \) is the inelastic mean free path of an electron moving from the overlayer.

\( \lambda_{B,A} \) is the inelastic mean free path of an electron from the substrate through the overlayer.

\( \theta \) is the angle between the surface normal and the analyzer slit exits.

Equations 2.2 and 2.3 are then plotted against \( t \) and the point where both lines meet is the thickness of the overlayer, A (in Figure2.5). In addition, the IMFP (\( \lambda \)) used for the thickness measurements were calculated from the TPP-2M equation[9]. During photoelectron process,
Figure 2.4, aside from the photoelectrons being emitted, Auger electrons could also be emitted as a result of the relaxation of the excited atoms.

2.3.2 Auger Electron Spectroscopy (AES)

AES is a surface sensitive technique used for the elemental and chemical compositional surface analysis of a sample and also for the identification of contaminants on the surface. It utilizes the emission of auger electrons in the Auger emission effect. An AES system is comprised of a UHV, an electron gun, detector and an energy analyzer. AES is a three electron process. Figure 2.6 shows a diagrammatic illustration of the Auger electron process. Here, the sample is bombarded by an electron beam of 1 keV-10 keV produced by an electron gun. This causes collision with the sample electron and then forms a hole in the K shell. As a result of the ejection of the K-shell core electron, the atom becomes unstable. Due to this instability, an electron from a higher energy level, L₁ fills this core vacancy releasing an energy in the form of a photon equal to the difference between the two energy levels. If this photon energy is higher than the binding energy of another higher level electron, L₃ within the atom, this energy will then be available for the escape of a third electron known as the Auger electron. An Auger electron has a kinetic energy (KE) which is characteristic of the parent atom.

The KE of the Auger electron is given by:

\[
KE = E_K - E_{L1} - E_{L2,3}
\]

\[\text{Equation 2.4}\]

![Figure 2.6. An illustration of the Auger electron process. [1].](image)
The final state of this atom is a double ionized atom with two holes. An auger excitation source could also be an x-ray.

AES is more surface sensitive than XPS with an electron escape depth of about 30-50 Å without losing all of its energy. This is due to the low KE of the auger electrons (10-3000 eV). The low escape depth is as result of the inelastic scattering an auger electron undergoes in a solid. During the auger emission process, secondary electron are generated giving rise to continuous increasing background signal making the actual auger peaks difficult to analyze. Hence, to better analyze auger data and remove the background signal, the spectrum is plotted in derivative mode, dN/dE versus KE rather than N(electron counts) versus KE. This is depicted in figure 2.7. The peak-to-peak heights in the derivative mode of the auger spectrum represents the surface concentration of a particular element.

![Auger spectrum of NiO(111) on Ru(0001) single crystal in derivative mode.](image)

**Figure 2.7.** Auger spectrum of NiO(111) on Ru(0001) single crystal in derivative mode.

2.3.3 Electron Energy Loss Spectroscopy (EELS)

EELS is a spectroscopy technique that measures electrons that undergo inelastic scattering. When done on the scale of eV, the technique help determine the surface states and surface electronic structure. As in AES, electrons are used to bombard the sample with a known kinetic energy. Some of the electrons undergo elastic scattering (without energy loss) while some
of the electrons undergo inelastic scattering losing energy as they travel in the solid and thus have their path deflected. The amount of energy loss is then measured by an energy analyzer and depending on the loss energy, the type of loss is known. In this work, the same set up for doing AES experiment is used for EELS. The only difference is that instead of measuring AES at 3 kV, EELS was done between 100 and 500 eV. The type of energy losses are the conduction band plasmons and surface phonons at around 100-1 meV, electronic interband transitions around 1-10 eV, surface Plasmon 10-50 eV and core level transitions around 10-1000 eV [10]. Figure 2.8 shows a typical inelastic scattering process. The EELS performed with high energy resolution but with low primary energies less than 20 eV, and energy resolution of a few meV, is called high resolution electron energy loss spectroscopy (HREELS) while that measured using primary energies between 100 and 500 eV is usually termed EELS. EELS can also be termed transmission EELS which involves the use of electrons emitted by a transmission electron microscope (TEM). The electrons used are in the range of 100 to 300 keV and it passes entirely through the material sample. Most of the measurements in this work were measured at primary energies in the 100 eV range, mainly to study the electronic structure of the surface, i.e. surface states.

Figure 2.8. Illustration of a typical inelastic process [10].
2.3.4 Low Energy Electron Diffraction Spectroscopy (LEED)

LEED is a surface characterization technique used to study the structure of the very few nanometers of a sample. It helps in determining the surface structure of crystalline surfaces. LEED is used qualitatively to analyze spot positions in determining the size, symmetry and the alignment of the overlayer with respect to the substrate. This is done by visualizing the diffraction patterns produced on the fluorescent screen as the electrons are backscattered from the sample surface. Quantitatively, it generates an intensity of spots versus electron beam energy which gives information on atomic positions.

The LEED system (figure 2.9) consists of an electron gun which produces the electrons, grids and fluorescent screen on which the diffracted pattern is observed. Monochromatic beam of electrons of low energy are emitted by cathode filament of the electron gun which is at a negative potential with respect to the sample. The energy of these electrons range from 20-300eV and accelerated and focused into a beam typically of about 0.1 to 0.5mm wide by a series of electrodes serving as electron lenses. These electrons are directed normal on the sample surfaces and some of the electrons are backscattered elastically while some inelastically. The detectors usually contains 3 to 4 hemispherical metal grids and a phosphor screen. The grids are used for screening out the inelastically scattered electrons. The first grid is held at ground potential and helps to separate the space above the sample from the retarding field so no field comes from other sources. The next grid also called the suppressor or gate is at a potential to stop or block low energy electrons. It is set to the retarding potential lower than the kinetic energy of the electrons produced by the electron gun, so it repels or blocks all inelastically scattered electrons.
This grid consists of 2 grids to make it mechanically more stable. The elastically scattered electrons are accelerated towards the screen at a high positive voltage (2kV -10kV). As these electrons impinge or strikes the fluorescent screen, they form bright spots whose pattern are the reciprocal of the ordered atoms of the surface. This pattern can be photographed for inspection or recorded by a video camera (CCD) for further analysis.

An example of a typical LEED image is shown in figure 2.10.

Figure 2.9. A schematic of a typical LEED system

Figure 2.10. The LEED image of a clean Ru(0001) on Al₂O₃
Incident electrons emitted by the electron gun is treated as waves according to the wave-duality nature of electrons. These waves are then scattered by regions of high electron density in the sample. The wavelength of the incident electron with a KE of 50 eV can be calculated by using the de Broglie’s wavelength equation leading to

\[ \lambda = \frac{6.63 \times 10^{-34} \text{ Js}}{2 \times 9.109 \times 10^{-31} \text{ kg} \times 50 \times 1.6 \times 10^{-19} \text{ J}}^{1/2} = 1.74 \text{Å} \]

This wavelength correspond to the interatomic distances in solids.

Figure 2.11 shows the interaction of the incident electrons with the atoms of interatomic distance \(a\). As shown in the diagram, the two adjacent atoms backscattered electrons at an angle and path difference, \(d\), between the electrons as they travel from the point of scattering to the detector. This diffraction pattern is partly described by Bragg’s law of diffraction which states that for constructive interference to occur, the path difference, \(d\) must be an integral multiple of the \(\lambda\) of the incident electron.

Therefore, \(\sin \theta = \frac{d}{n\lambda} \)  

\[ \text{Equation 2.10} \]

where \(n=1, 2, 3, 4\ldots\)
2.3.5 Atomic Force Microscopy (AFM)

The Ru(0001) films used as the substrates upon which the oxides were grown and the magnetic oxides are characterized by AFM to determine the surface roughness. AFM measurement can be done in contact mode or tapping mode. An AFM consists of a cantilever with tips, diode laser, piezoelectric motor, and a photodetector. An AFM uses a cantilever with a very sharp tip (SiN used for these experiments) to scan over a sample surface. As the tip approaches the surface, the close range attractive forces between the surface and the tip causes the cantilever to bend towards the surface. However, as the cantilever is brought even closer to the surface, increasingly repulsive forces makes the cantilever to bend away from the surfaces.

An AFM has a z-scanner that moves the cantilever up and down and xy scanner that moves the sample back and forth underneath the cantilever, and the position detector that records the bending of the cantilever. The position sensor works by tracking of the laser beam that is reflected from the top of the cantilever. Any bending in the cantilever will cause a change in the direction of the reflected beam. The position detector then tracks those beam changes; all as potentials or voltages. Using the detection method explained, the AFM measures the topography of a sample surface by scanning the cantilever over a region of interest. The raised and lowered features of the sample surface influence the bending of the cantilever measured by the detector. It then generates a topography map of the surface by using a feedback loop to control the height of the tip above the surface. The AFM was performed ex-situ in this work. AFM roughness value is measured as a root mean square value in nanometers. The lower the RMS value, the smoother the film surface. The schematic of an AFM is shown in figure 2.12. Figure 2.13 also showed a typical topography image of a Ru(0001) surface with root mean square roughness value of less than 1 nm.
2.4 References


CHAPTER 3
GROWTH OF Co$_3$O$_4$(111) AND CoO(111) ON Ru(0001) BY MOLECULAR BEAM EPITAXY$^1$

3.1 Introduction

Polar oxide surfaces are of broad and long-standing interest in multiple areas, including catalysis [1–5], battery technology [6], and magnetic applications [7,8]. Additional interest arises from our recent demonstration of direct graphene growth on nanoscale-thickness Co$_3$O$_4$(111) films on Co(0001) [9,10] and evidence, to beyond 400 K, of substrate-induced spin polarization in graphene domains[11]. The growth of Co$_3$O$_4$(111) films for “spintronic” beyond-CMOS device applications, are of considerable interest. Growth is far from sufficient as along with relevant boundary polarization and electronic properties, other characteristics such as the surface roughness and dielectric-breakdown strength, are therefore also important.

We focus here on conditions for Co$_3$O$_4$(111) growth on Ru(0001), to film thicknesses well beyond 1 nm. Previous studies have reported on Co$_3$O$_4$(111) growth on Al$_2$O$_3$(0001) [12,13], or on Ir(100) [14–16]. Ru, however, is a material of general interest and exhibits compatibility with CMOS[17] and two-dimensional materials device applications[18]. It is thermally and chemically stable, and does not alloy with Co, thus making it suitable as a substrate for graphene/cobalt oxide applications. We also present here the first information on the surface roughness and dielectric-breakdown strength of these films. Results presented here demonstrate that molecular beam epitaxy (MBE) of Co on Ru(0001) at 500 K results, at higher O$_2$ background pressures (1 x 10$^{-4}$ Torr), in the formation of Co$_3$O$_4$(111), and, at lower pressures

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$^1$This chapter is modified from Opeyemi Olanipekun; Chad Ladewig; Jeffry Kelber; Michael Randle; Jubin Nathawat; Chun-Pui Kwan; Jonathan P Bird; Priyanka Chakraborti; Peter A Dowben; Tao Cheng; William A Goddard III. Epitaxial growth of Cobalt oxide phases on Ru(0001) for spintronic device applications. Submitted to IOP journal (2017).
(7.5 \times 10^{-7} \text{Torr}), in the formation of CoO(111). The two oxide phases are marked by distinctive x-ray photoemission (XPS), low energy electron diffraction (LEED), and electron energy loss (EELS) spectra. The root mean square (rms) roughness of the Co$_3$O$_4$(111) surface, determined by atomic force microscopy (AFM), is < 1 nm, and the dielectric breakdown strength in air is ~1.0 MV/cm. These data therefore demonstrate the suitability of Co$_3$O$_4$ films for a variety of low-voltage, advanced-device applications.

3.2 Experimental Methods

The cobalt oxide film growth and \textit{in-situ} characterization were carried out in a vacuum system with three interconnected chambers, isolated by manual gate valves: (i) an introduction chamber connected to a turbo-molecular pump (base pressure: 10^{-8} \text{Torr}); (ii) an MBE chamber connected to a turbo-molecular pump (base pressure: 5 \times 10^{-10} \text{Torr}), with capabilities for deposition and sample heating (300 – 1100 K) in reactive environments, and; (iii) an analysis chamber pumped with an ion/titanium sublimation pump combination (base pressure: 5 \times 10^{-11} \text{Torr}). The analysis chamber is equipped with an unmonochromatized dual-anode x-ray source and double-pass cylindrical mirror analyzer with coaxial electron gun, permitting acquisition of XPS, Auger electron spectroscopy (AES) and EELS data. The chamber is also equipped with a reverse-view LEED I(V) system. Sample transport between chambers was accomplished with a magnetically-coupled feedthrough. Pressures in all chambers were monitored with nude ion gauges, calibrated for N$_2$, and O$_2$ exposures, and were controlled with a manual leak valve using electronic grade O$_2$.

3.2.1 Ru(0001) Film Growth

Ru(0001) films were formed by magnetron sputter deposition at 700 K in an Ar plasma (3.5 mTorr, 15 W), on commercially available Al$_2$O$_3$(0001) 1 cm $\times$ 1 cm substrates. Prior to
deposition, the alumina substrates were cleaned by annealing in O\textsubscript{2} (1000 K, 10\textsuperscript{-7} Torr). Deposited films exhibited typical sample roughness values < 1 nm and Ru thickness values of ~500 Å or less, as determined by ex-situ AFM and x-ray reflectivity measurements. Films were then transferred in air to the multichamber system for MBE and surface analysis. Ru films were annealed in O\textsubscript{2} and in UHV at 1000 K to remove C and O, until they exhibited a sharp 1 × 1 LEED pattern. The presence of C was determined by measuring the ratio of the positive-going peak to the negative-going peak near 273 eV, with a clean Ru surface exhibiting a ratio of ~0.78 [19].

3.2.2 Cobalt Oxide Film Growth

Cobalt oxide films were grown on Ru(0001) substrates at 500 K in an O\textsubscript{2} environment (figure 3.1). Co MBE was accomplished using a commercial electron-beam evaporator and a Co rod source. Studies were carried out at two different O\textsubscript{2} partial pressures, 10\textsuperscript{-4} and 7.5 × 10\textsuperscript{-7} Torr. Oxide film average thickness was determined as a function of Co deposition time by XPS measurements of relative Co 2p and Ru 3d intensities[20], and using a calculated Ru photoelectron inelastic mean free path length of 18.5 Å [21,22]. This allowed measurements of films to thicknesses of ~100 Å, beyond which point the Ru substrate XPS signal was completely attenuated. Film thicknesses, at longer growth times, were estimated by extrapolation of the growth rate derived for thinner films.
3.2.3 XPS, AES and EELS Measurements

XPS data were acquired with the double pass analyzer in constant-pass energy mode, with Mg Kα radiation from the unmonochromatic dual anode source (operated at 15 kV and 300 W). AES spectra were acquired with an electron-beam energy of 3 keV in integral mode, and differentiated by computer.

EELS spectra were acquired at 100 eV electron beam energy, unless otherwise specified, in reflection mode. Analyses of XPS and AES spectra were carried out by standard methods [20] using commercial software.

3.2.4 LEED

The analysis of LEED data was carried out using LEED images digitized with commercial software. This allowed measurements of Co oxide domain sizes by determination of the full-width-at-half-maximum (FWHM) of the appropriate LEED diffraction spots [23]. The domain size determination was performed by Dr. Peter Dowben’s group at the University of Nebraska, Lincoln.
3.2.5 AFM

Atomic-force microscopy of the Co oxide films was performed in tapping mode using a Bruker Dimension Icon, capable of nanoscale surface topography and morphology measurements of a range of different surface types. This was done by our collaborator, Dr. Jonathan Bird’s group.

3.2.6 Electrical Measurements

Dielectric breakdown of the Co oxide films was explored using a Signatone probe station equipped with W microtips with a tip diameter of <50 μm. DC voltages were sourced with a Keithley 2400 source-measure unit, which was also used to measure the resulting leakage current flowing in response to the applied voltage. This was also done by our collaborator, Dr. Jonathan Bird’s group.

3.3. Results

Growth and surface analysis results are presented first for Co MBE in an environment of $7.5 \times 10^{-7}$ Torr $O_2$. Subsequently, corresponding data are presented for films grown in $10^{-4}$ Torr of $O_2$. Finally, AFM and current-voltage (I-V) measurements indicating dielectric breakdown and hysteresis are shown for films grown at the higher $O_2$ pressure.

3.3.1. Cobalt Oxide Growth at Low $O_2$ Pressure: CoO(111)

LEED data are displayed in figure 3.2 for (a) a clean Ru(0001) film and (b,c) cobalt oxide films of increasing thickness. Corresponding LEED-spot profiles are shown in figures 1d-f, with XPS and EELS data are displayed in figure 3.3. The LEED data show that the new Co-oxide lattice is azimuthally in registry with that of the Ru(0001) substrate (figure 3.2b). Taking the Ru
LEED data as indicating an in-plane lattice constant of 2.7 Å yields a lattice constant for the oxide of ~3.0 Å, consistent with the formation of CoO(111) [14]. The diffraction spot size visibly decreases with increasing oxide thickness (figure 3.2b,c), indicating that oxide-film average domain size increases as the growth proceeds. An analysis of the FWHM for a 370 Å thick film (figure 3.2c) indicates an average domain size of 27 (±2) nm.

The XPS Co 2p spectra (figure 3.3a) do not change significantly with increasing film thickness. The somewhat complex satellite structure is characteristic of CoO [5,24,25]. The corresponding O 1s spectra (figure 3.3b) — which remain unchanged at all film thicknesses — indicate two O 1s chemical environments. The main peak, centered near 530.0 eV binding energy, is consistent with earlier reports for the binding energy of lattice O in the oxide, while
the higher-energy feature indicates surface hydroxylation [26]. The (111) surfaces of polar oxides with the rock salt structure, such as CoO, are prone to reconstruction (at or near room temperature), due to the unstable Madelung energy [6,27]. Surface hydroxylation, however, reduces surface polarization, and can stabilize the (111) surface [26,28]. EELS spectra acquired at 100 eV primary energy (figure 3.3c) demonstrate that the EELS loss spectrum remains constant over a broad range of thicknesses. The rate of thickness increase with deposition time (figure 3.3d) is constant over the thicknesses measured. The observed ~2 eV transition is consistent with previous reports on CoO particles [29].

**Figure 3.3.** The (a) Co(2p) XPS spectra of CoO(111). 20-Å thick film (black); 67-Å thick film (red); 600-Å thick film (blue). (b) O 1s XPS spectra of CoO(111) for 67-Å film, decomposed into components for the oxide and (at higher binding energy) OH; (c) EELS spectra of CoO films of varying thickness: 20 Å (red); 38.5 Å (green); 52 Å (blue); 67 Å (black). (d) the XPS-derived CoO(111) thickness as a function of deposition time at 500 K.
3.2 and 3.3) are entirely consistent with the formation of a CoO(111) film at lower O₂ partial pressure. The average domain size and electronic structure of the film remain constant over a broad range of film thicknesses. Reconstruction of this film is not observed, and this is attributable to the observed (figure 3.3b) surface hydroxylation.

3.3.2. Cobalt Oxide Growth at High O₂ Partial Pressure: Co₃O₄(111)

The LEED images are displayed in figure 3.4a for a 6.8Å thick Co₃O₄(111) film on Ru(0001) substrate, figure 3.4b for a 16.6 Å thick Co₃O₄(111) film on Ru(0001) substrate, in figure 3.4c for a 22.9Å thick film, figure 3.4d for a 100 Å thick film and figure 3.4e for a 280 Å thick Co₃O₄(111) film grown by MBE under the same conditions as for CoO, except with the background O₂ pressure of 10⁻⁴ Torr. Corresponding diffraction spot profiles are displayed in figures 3.4f-j. The cobalt oxide LEED images (figure 3.4d) indicate two 6-fold patterns rotated 30° with respect to each other. Similar rotated patterns have been reported for Co₃O₄(111) grown directly on Al₂O₃(0001), indicating twinning of the film [13,16]. In contrast, only a single 6-fold pattern was observed for cobalt oxide films grown at lower O₂ pressure. Analysis of the FWHM of the diffraction spots for the 280 Å film (figure 3.4e,j) indicate a domain size of 13.5 (3) nm. The LEED data indicate that the primary Co₃O₄(111) lattice is in azimuthal registry with that of the Ru(0001) substrate. The reciprocal space unit cells for the Ru(0001) lattice and for the Co₃O₄(111) lattices (figure 3.4b,g) indicate an in-plane Co₃O₄(111) direct lattice constant slightly greater than twice the Ru(0001) lattice constant, ~5.65 Å, consistent with a reported value of 5.7 Å [16].

The evolution of Co₃O₄ Co 2p and O 1s XPS data are displayed in figures 3.5a,b, respectively. EELS data are displayed in figure 3.5c. The Co 2p spectrum of the oxide evolves with average film thickness (figure 3.5a). For film thicknesses > ~ 20 Å, the Co(2p) spectrum is
in close agreement with those previously published for Co$_3$O$_4$(111) single crystals [5,24,25] and nanocrystalline films [30], with Co 2p$_{3/2}$ and Co 2p$_{1/2}$ features near 780 eV and 795 eV, and a satellite feature (figure 3.5a, arrow) near 790 eV. Films with average thicknesses < 20 Å, however, exhibit Co 2p spectra resembling that of CoO (Fig. 3a) [5,24,25].

Figure 3.4. The evolution of LEED images with Co$_3$O$_4$(111) film of varying thickness on Ru(0001). (a) 6.8 Å thick Co$_3$O$_4$ (b) 16.6 Å (111) film; (c) 22.9 Å (d) 100 Å thick Co$_3$O$_4$(111) film, and (e) 280 Å thick Co$_3$O$_4$(111) film. Corresponding linescan profiles are shown in (f), (g), (h) and (j), respectively. The different oxide reciprocal lattices that are indicative of twinning are shown by solid and dashed triangles in (b). The LEED beam energy is 60 eV.
In contrast to the Co 2p spectra, O 1s spectra (figure 3.5b) exhibits no significant change with film thickness, and indeed are very similar to those observed for CoO(111) films (figure 3b).

The main O 1s feature near 529 eV binding energy has been assigned to lattice O, while the broader feature at higher binding energy has been demonstrated, by comparison with vibrational spectra and H₂O exposure studies to be due to surface hydroxylation [5]. The EELS spectra (figure 3.5c) show an evolution with film thickness similar to that observed for Co 2p spectra (figure 3.5a). At average film thicknesses < 20 Å, a small single loss feature near 2 eV may be discerned, with a larger more intense feature near 7 eV. In contrast, films > 20 Å thick exhibit a dual loss feature at 2.1 eV and 3.0 eV, as well as the larger loss feature at ~ 7 eV. The observation of two interband transitions at 2.1 eV and 3.0 eV is consistent with optical measurements on non-epitaxial Co₃O₄ films, which indicate two main transitions, the energies of which vary with experimental conditions of deposition and film microstructure [31,32]. The EELS data in figure 3.5c therefore corroborate the Co 2p XPS data indicating an evolution of Co oxide film structure and composition with average film thickness.
3.3.3 AFM

An ex-situ AFM image is shown in figure 3.6 for a 100 Å thick Co$_3$O$_4$(111)/Ru(0001) film.

![AFM Image](image)

**Figure 3.6.** The AFM image of Co$_3$O$_4$(111)/Ru(0001) film of 100-Å average oxide thickness, with corresponding line scan. The inset shows the topography variation measured over an area of 20 µm × 20 µm. The white dashed line indicates the path followed in the main panel (Courtesy of Dr. Bird’s group).

The 20 µm x 20 µm image (figure 3.6) indicates a general surface roughness corrugation < 1 nm. There are irregular local features of considerable height, but these are likely particulates adsorbed during *ex-situ* handling.

3.4. Electrical Breakdown Characteristics

In figure 3.7, we present representative current-voltage characteristics, measured by placing one tip of our probe station on the Co$_3$O$_4$ surface and the other on the underlying Ru substrate. This measurement therefore probes the breakdown of the films and leads to behavior exemplified by that of figure 3.7. The main panel of this plot shows data collected in a set of (four) different voltage sweeps; in the first portion (1.) of the measurement, the current remains essentially quenched (note the behavior shown in the inset) up to a voltage of ~1.2 V, at which point a dramatic onset is observed. This breakdown occurs at a field of ~1 MV/cm, indicative of
the high dielectric quality of the grown film. Following this sweep, the voltage was then cycled back and forth (2. & 3.), over which range clear evidence of resistive switching is observed. While the details of this require further study, we note that this memristor-like behavior is typical of resistive switching in oxides [33].

![Graph](image)

**Figure 3.7.** The breakdown and resistive switching data for Co$_3$O$_4$/Ru(0001). Insert: close up of flat-band region near 0 V applied bias (Courtesy of Dr. Bird’s group).

3.5 Discussion

The data in figures 3.2 and 3.3 demonstrate conclusively that the oxide film grown at an O$_2$ pressure of $7.5 \times 10^{-7}$ Torr is CoO(111), while the data in figures 3.4 and 3.5 demonstrate that films grown under identical conditions, but at an O$_2$ pressure of $10^{-4}$ Torr, are Co$_3$O$_4$(111)—but only at thicknesses greater than ~20 Å. The two films are marked by distinctive Co (2p) spectra, as shown in detail in figure 3.8. The Co 2p spectrum of CoO(111) (figure 3.8a) exhibits a broad Co 2p$_{3/2}$ feature with a peak at 780.1 eV, due to Co(II), but broadened by a satellite feature, in excellent agreement with previous results [25,26]. In contrast, the corresponding feature for Co$_3$O$_4$ exhibits a sharper peak centered near 779.8 eV due to the presence of both Co(III), and a Co(II) feature at slightly higher binding energy [25,30]. A comparison of the data
in figure 3.8 to the XPS data in figure 3.5a indicates that Co$_3$O$_4$(111) film growth under these conditions begins with the formation of Co(II) oxides, without significant Co(III) observed until the average oxide film thickness exceeds $\sim$ 20 Å.

The EELS data (figure 3.5c) show a similar trend, and the LEED data (figure 3.4) indicate an absence of twinning for films < 20 Å thick. A similar trend regarding twinning has been reported for the LEED images of Co$_3$O$_4$(111) films grown by O radical-assisted MBE directly on Al$_2$O$_3$(0001), but the corresponding Co(2p) XPS data in that case indicate the presence of Co(III) species on that substrate even at the earliest stages of film growth, with thicknesses much less than 20 Å [12]. This strongly suggests different Co$_3$O$_4$ growth mechanisms on Ru(0001) compared to Al$_2$O$_3$(0001).

A possible explanation for the different trends in evolution of Co 2p XPS spectra for Co$_3$O$_4$ film growth on Ru compared to alumina is that, as Co(III) films occupy octahedral sites in the oxide [9], such sites are not plentiful for oxide growth on Ru at average thicknesses $< \sim$ 20 Å. This would in turn imply that oxide growth on Ru under these conditions is layer-by-layer, at

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**Figure 3.8.** The Co(2p) XPS spectra of (a) 67Å thick CoO(111); (b) 100 Å thick Co$_3$O$_4$(111) film
least at low thicknesses, and that Co$_3$O$_4$(111) growth on alumina follows a Stransky-Krastanov (SK) or Frank van der Merwe (FM) growth mechanism. Indeed, the authors suggest just such a growth mechanism on Al$_2$O$_3$(0001), but with the possible formation of a Co$_2$O$_3$ phase at very low thicknesses [12].

The complex LEED pattern observed for thicker Co$_3$O$_4$(111) film growth on Ru(0001), consisting of two six-fold patterns rotated by 30$^\circ$ from each other, (figures 3.4b,c,d) is similar to those reported for Co$_3$O$_4$(111) growth by various methods on Ir [16] and on Al$_2$O$_3$(0001)[12,13,34] for Fe$_3$O$_4$(111) on Pt(111) or Ru(0001)[3]. This behavior is indicative of twinning[12,13,34] and appears to be a general phenomenon for both Co$_3$O$_4$(111) and Fe$_3$O$_4$(111), regardless of substrate or growth method.

Both CoO(111)/Ru(0001) and Co$_3$O$_4$(111)/Ru(0001) films could be heated to at least 900 K in UHV without any detectable change in XPS, LEED or EELS spectra. Such thermal stability is unusual, as polar oxide surfaces, such as CoO(111) (rocksalt structure) [16,35], but also Co$_3$O$_4$(111) [16] are known to reconstruct at even moderate temperatures in UHV. Such surfaces, however, are stabilized by surface hydroxylation [28,35]. XPS O 1s spectra (figures. 3b, 5b) indicate such surface hydroxylation for both oxide phases under these growth conditions. Such hydroxylation has also been reported for both CoO(111) [26] and Co$_3$O$_4$(111) [5] surfaces prepared under UHV conditions. Since DFT calculations [9] indicate that the surface region of the relaxed unhydroxylated Co$_3$O$_4$(111) is entirely composed of Co$^{2+}$ cations, the distinctive XPS Co 2p spectra (figures 3.3a, 3.5a), and surface sensitive EELS spectra (figures 3.3c, 3.5c), indicate distinctive electronic structures in the surface region of each film. Therefore, the data here confirm that both films are essentially unreconstructed and bulk-terminated under these conditions due to surface hydroxylation.
The suitability of Co$_3$O$_4$(111) films for device applications is indicated by the AFM (figure 3.6) and electrical-resistivity data (figure 3.7). The large-area AFM data indicate that the typical surface roughness is $\sim$ 1 nm or less, certainly suitable for subsequent thin-film growth. A dielectric breakdown strength of 1 MV/cm is extremely promising for a variety of low-voltage applications, and there may also be potential interest in using these films for applications, including resistive-switching based memory technology [36] (figure 3.7). The ability, however, to support direct graphene growth [9,11,37], and possibly the growth of other 2D materials, on Co$_3$O$_4$(111), broadens potential device applications. Indeed, previously reported results for graphene growth on MgO(111), including the observation of an oxidized initial C layer [38], suggest the potential for graphene deposition on similarly-structured CoO(111), as well.

3.6 Summary and Conclusions

The data presented here demonstrate that Co MBE, performed at 500 K and under UHV conditions on a Ru(0001)/Al$_2$O$_3$(0001) substrate, yields CoO(111) at a background O$_2$ pressure of $7.5 \times 10^{-7}$ Torr, and Co$_3$O$_4$(111) under identical growth conditions except for a background pressure of $10^{-4}$ Torr. Co$_3$O$_4$(111) formation, including the observation of twinning (LEED), the presence of Co(III) in the Co 2p XPS spectrum, and characteristic EELS spectra, are only observed under such growth conditions for Co$_3$O$_4$(111) films with average thickness above 20 Å. Both oxide phases are hydroxylated under these deposition conditions, and show no evidence of reconstruction. Both oxide phases are stable upon annealing to 900 K in UHV, without observable changes to XPS, LEED or EELS spectra. The Co$_3$O$_4$(111) film has an AFM-determined average surface roughness of less than 1 nm, and a dielectric breakdown voltage of $\sim$1 MV/cm, while also showing evidence of resistive switching. Co$_3$O$_4$(111) films are therefore suitable for a variety of device applications, including potential graphene/spintronic applications.
3.7 Funding

Work at UNT/UB/UNL was supported by the NSF under grant no. ECCS-1508991/ECCS-1509221/ECCS-1508541. Work at Caltech was supported by NSF DMR-1436985.

3.8 References


[35] H. Kuhlenbeck, H. Freund, Hydroxyl groups on oxide surfaces: NiO (100), NiO (111),


CHAPTER 4

GROWTH OF FEW LAYER GRAPHENE ON CoO (111) AND Co$_{0.5}$Fe$_{0.5}$O (111) BY FORMATION OF A GRAPHENE OXIDE BUFFER LAYER WITH C$^{3v}$ SYMMETRY$^2$

4.1 Introduction

Graphene devices require a dielectric substrate, while better on/off device performance typically requires converting graphene from a gapless semiconductor to a more conventional semiconductor$^[1]$. Scalable device fabrication, so as to open a band gap through symmetry breaking$^[1–15]$ demands epitaxial growth on dielectric substrates by scalable methods. While graphene/substrate lattice matching is normally a major consideration in epitaxial growth$^[16–19]$, the demonstration of layer-by-layer graphene growth on incommensurate Co$_3$O$_4$(111)/Co$^[20]$ and resulting oxide-induced spin polarization of graphene domains$^[21]$ demonstrate that large-domain graphene growth on incommensurate magnetic oxides is both feasible and a route to substrate-induced graphene spin polarization—spintronics without spin injection. Recent experimental and theoretical results$^[22]$ indicate that a key step in graphene growth on Co$_3$O$_4$(111) is formation of a graphene oxide “buffer layer” between the cobalt oxide substrate and subsequently grown graphene overlayers, with significant graphene-to-cobalt oxide charge transfer. The proposed mechanism for graphene formation on Co$_3$O$_4$(111) also suggests the extension of this model to other oxides supporting graphene-to-substrate charge transfer$^[22]$. This category would include other p-type oxides, such as CoO(111), but does exclude Cr$_2$O$_3$(0001)$^[22]$, for which calculations indicate oxide-to-graphene charge transfer is favored$^[23]$. We report here graphene growth by C MBE on OH-terminated CoO(111) via formation of

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$^2$ Work done in this chapter was in collaboration with Dr. Jonathan Bird Group (University of Buffalo, New York) and Dr. Peter Dowben Group (University of Nebraska, Lincoln).
a graphene oxide buffer layer, with similar results for growth on OH-terminated Co$_{0.5}$Fe$_{0.5}$O(111). Graphene layers form on top of the graphene oxide layer.

4.2 Experimental

Cobalt oxide film growth and *in-situ* characterization were carried out in a vacuum system with three interconnected chambers, isolated by manual gate valves: (i) an introduction chamber connected to a turbo-molecular pump (base pressure: 10$^{-8}$ Torr); (ii) an MBE chamber connected to a turbo-molecular pump (base pressure: 5 × 10$^{-10}$ Torr), with capabilities for deposition and sample heating (300 – 1100 K) in reactive environments, and; (iii) an analysis chamber pumped with an ion/titanium sublimator pump (base pressure: 5 × 10$^{-11}$ Torr.) The analysis chamber is equipped with an unmonochromatized dual-anode x-ray source and double-pass cylindrical mirror analyzer with coaxial electron gun, permitting acquisition of XPS, Auger electron spectroscopy (AES) and EELS data. The chamber is also equipped with a reverse-view LEED I(V) system. Sample transport between chambers is accomplished with a magnetically-coupled feedthrough. Pressures in all chambers are monitored with nude ion gauges, calibrated for N$_2$, and O$_2$ exposures, and were controlled with a manual leak valve using electronic grade O$_2$.

XPS data were acquired with the analyzer in constant pass energy mode with an unmonochromatized Alkα source operated at 15 keV, 300 W. XPS acquisition after C deposition was minimized, as inspection indicated x-ray-induced chemistry at the C/oxide interface upon extensive exposure to x-rays. AES spectra were acquired in integral (N(E) vs. E) mode at 3000 eV primary excitation energy, and differentiated by computer. EELS spectra were acquired at 100 eV primary excitation energy. XPS and AES spectra were analyzed by standard methods [24].
Raman spectra and Raman maps were acquired using a 488 nm excitation source at varying laser power. The measurements are performed using a 100x microscope objective lens with an automated x-y-z stage having a step size of 100 nm. For Raman mapping an area of 20 μm x 20 μm was scanned at the center of the sample with a step size of 0.25 μm. All measurements were performed at ambient temperature under controlled humidity.

Analysis of LEED data was carried out using LEED images digitized with commercial software. This allowed measurements of oxide and graphene domain sizes by determination of the full-width-at-half-maximum (FWHM) of the appropriate LEED diffraction spots [25].

4.2.1 Ru(0001) Film Growth.

Ru(0001) films were formed by magnetron sputter deposition at 700 K in an Ar plasma (3.5 mTorr, 15 W), on commercially available Al2O3(0001) 1 cm × 1 cm x 1 mm substrates, in a separate sputter deposition chamber. Prior to deposition, the alumina substrates were cleaned by annealing in O2 (1000 K, 10⁻⁷ Torr). Deposited films exhibited typical sample roughness values < 1 nm and Ru thickness values of ~ 500 Å or less, as determined by ex-situ AFM measurements and x-ray reflectivity respectively (XRR). Films were then transferred in air to the multichamber system for MBE and surface analysis. Ru films were annealed in O2 and in UHV at 1000 K to remove C and O, until they exhibited a sharp 1 × 1 LEED pattern. The presence of C was determined by measuring the ratio of the intensities of the positive-going to negative-going AES features near 273 eV (in derivative mode), with a clean Ru surface exhibiting a ratio of ~ 0.78 [26].

4.2.2 CoO(111) and Co0.5Fe0.5O(111) Film Growth

CoO(111) films were deposited by Co MBE at 500 K on Ru(0001) in an O2 pressure of
7.5 x 10^{-7} \text{Torr}, as described previously\[27\]. Film thickness was determined by measuring the attenuation of the Ru 3d substrate intensity as a function of Co deposition time to a limit of ~ 100 Å. Larger film thicknesses were estimated by extrapolation of this growth curve. The Co_{0.5}Fe_{0.5}O(111) film was formed by first depositing a CoO film as described. Subsequently, Fe was deposited on the CoO film at 700 K at 5 \times 10^{-5} \text{Torr} \text{O}_2. The composite film was then annealed at 800 K in 5 \times 10^{-5} \text{Torr} \text{O}_2. \text{CoO(111)} and \text{Co}_{0.5}\text{Fe}_{0.5}\text{O(111)} film thicknesses used for graphene growth were estimated at 600 Å and 100 Å, respectively.

**Figure 4.1.** (a) Co 2p XPS spectra of 600Å CoO(111)/Ru(0001) film (b) O 1s XPS spectra of 600Å CoO(111)/Ru(0001) film with deconvolution of peaks.
LEED data exhibited the same expected LEED pattern for both films [27–29]. XPS data (figures 4.1 and 4.2) indicated the presence of Co$^{+2}$ for the CoO film and Co$^{+2}$ and Fe$^{+2}$ for the Co$_{0.5}$Fe$_{0.5}$O(111) films [30]. The Co/O atomic ratio in the CoO film, and the (Co+Fe)/O atomic ratio in the Co$_{0.5}$Fe$_{0.5}$O(111) film were both 1:1. O 1s XPS also indicated both films to be OH-terminated as shown in figures 4.1b and Fig 4.3.

Figure 4.2. (a) Fe 2p XPS spectra of Co$_{0.5}$Fe$_{0.5}$O(111)/Ru(0001) film (b) Co 2p XPS spectra of Co$_{0.5}$Fe$_{0.5}$O(111)/Ru(0001) film.

Figure 4.3. O 1s XPS spectra of Co$_{0.5}$Fe$_{0.5}$O(111) showing deconvolution of peaks.
4.2.3 Graphene Film Growth

The graphene films were deposited by MBE from a carbon rod source at a working pressure of $5 \times 10^{-10}$ Torr. The films were deposited on CoO(111) substrates at 800 K. A similar deposition on the Co$_{0.5}$Fe$_{0.5}$O(111) resulted only in loss of lattice O, with no C deposition. Therefore C was deposited on Co$_{0.5}$Fe$_{0.5}$O(111) at room temperature, followed by annealing to 600 K in UHV. Graphene film thickness was estimated from AES or XPS spectra assuming an interlayer equivalent thickness of 3.3 Å per graphene monolayer (ML) [31].

4.3 Results

4.3.1 Graphene on CoO(111)/Ru(0001)

AES and EELS data are shown in figure 4.4 for CoO(111)/Ru(0001) before (a,b) and after (c,d) deposition of ~ 2.5 ML C at 800K, followed by annealing at that temperature in UHV. Prior to C deposition, XPS (figure 4.1a) indicates a O/Co atomic ratio of 1.1 with (figure 4.4b) an interband transition near 2.0 eV, in agreement with previous reports [30]. After C MBE and annealing in UHV at 800 K (figure 4.4c), a C overlayer of ~ 2.5 ML average thickness was observed. The AES lineshape is indicative of sp$^2$ C [32]. The corresponding EELS spectra (figure 4.4d) indicate a prominent loss feature near 6.0 eV. A comparison with ellipsometry results for graphene/Co$_3$O$_4$(111)/Co(0001) [20] and for EELS spectra of few layer graphene on SiC [33] identifies this as the $\pi$ to $\pi^*$ transition. The peak energy near 6 eV, as opposed to ~ 5.2 eV for bilayer graphene on SiC [33] indicates graphene to cobalt oxide charge transfer.

The LEED images were acquired before and after C MBE and annealing at 800 K are shown in figure 4.5a and b, respectively. Importantly, after C MBE but prior to additional
Figure 4.4. (a) AES and (b) EELS data for ~ 600 Å thick CoO(111)/Ru(001) film prior to C deposition. (c) and (d) Corresponding data after C MBE and annealing at 800 K in UHV.

Figure 4.5. LEED spectra of (a) ~600Å CoO(111) film; (b) 2.5ML of graphene film on~600Å CoO(111)/Ru(0001) after C MBE and anneal at 800K. LEED data were acquired at 86eV.
annealing, no LEED pattern was apparent. Annealing at 800 K therefore induces sufficient long-range order in the C layer to observe a LEED pattern with relatively broad diffraction spots, but with no change in AES intensity (not shown), indicating that LEED pattern observed in figure 4.5b is indicative of ordered sp$^2$ C—graphene. As shown in Table 4.1, prior to C deposition, the CoO(111) average domain size is $\sim$ 27 nm, with the expected C$_{6V}$ symmetry. The C deposition and annealing yields a graphene average domain size of only $\sim$ 8 nm. Importantly, however, the symmetry has now been reduced to C$_{3V}$ (Table 4.1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average A site intensity (arb. units)</th>
<th>Average B site intensity (arb. units)</th>
<th>Symmetry</th>
<th>Domain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoO(111)</td>
<td>183</td>
<td>185</td>
<td>C$_{6V}$</td>
<td>27±2 nm</td>
</tr>
<tr>
<td>C/CoO(111)</td>
<td>167</td>
<td>160</td>
<td>C$_{3V}$ (4.5%)</td>
<td>8±3 nm</td>
</tr>
<tr>
<td>Co$<em>{0.5}$Fe$</em>{0.5}$O(111)</td>
<td>207</td>
<td>207</td>
<td>C$_{6V}$</td>
<td>5.5±2 nm</td>
</tr>
<tr>
<td>C/Co$<em>{0.5}$Fe$</em>{0.5}$O(111)</td>
<td>187</td>
<td>175</td>
<td>C$_{3V}$ (6.4%)</td>
<td>5±2 nm</td>
</tr>
</tbody>
</table>

Table 4.1. Summary of LEED intensity and domain analyses for CoO(111) and Co$_{0.5}$Fe$_{0.5}$O(111) before and after C deposition. LEED data for CoO(111) and Co$_{0.5}$Fe$_{0.5}$O(111) were acquired at 86 eV and 60eV beam energy respectively. A symmetry of C$_{6v}$ may be just multiple domains and is no certain indicator of higher symmetry. LEED domain sizes and symmetry determination was carried out by Dr. Dowben’s group at the University of Nebraska, Lincoln.

Representative Raman spectra for the 2.5 ML graphene/CoO(111) sample are displayed in figure 4.6 as a function of increasing laser power. The spectra exhibit the broad, intense D and G features, and the complex 2D spectrum near 2800 cm$^{-1}$ that are collectively characteristic of graphene oxide [34]. (The origin of the very sharp feature near 2400 cm$^{-1}$ is remains unknown at present, but appears systematically in all traces.) The data in figure 4.6 do not indicate the
absence of unoxidized graphene in a second layer, as a small, sharper D feature and a 2D peak near 2700 cm$^{-1}$ indicative of graphene would be obscured by the graphene oxide spectrum [34]. Raman mapping was carried out to examine the uniformity of the intensities of the D, G and 2D features shown in figure 4.6. Raman mapping results are shown in figure 4.7a,b and c for the D, G and 2D features, respectively. The results indicate a high degree of uniformity for all three features over ~ micron length scales. However, there are discrete regions indicating high intensities for all the Raman peaks. These may be related to discrete regions of topographical roughness as determined by ex-situ AFM data (figure 4.8). While much of the surface is smooth (rms ~ several nm or less), certain features are observed with heights > 100 nm. Whether such features are a result of evolving surface roughness during cobalt oxide film growth or result from
Figure 4.7. The Raman mapping data for (a) the D peak, (b) the G peak and (c) the 2D peak as shown in Fig.4.6.

Figure 4.8. The AFM image and cross section for sample consisting of 2.5 ML graphene/graphene oxide on CoO(111) film 600 Å thick.
e. g., ex-situ particulate contamination cannot be determined from the existing data.

4.3.2 Graphene on Co$_{0.5}$Fe$_{0.5}$O(111)/Ru(0001)

AES and EELS spectra before C deposition and after deposition of 4.2 ML C at room temperature, followed by annealing to 600 K in UHV, are compared in figure 4.9. Corresponding LEED data are displayed in figure 4.10.

**Figure 4.9.** (a) AES and (b) EELS spectra of Co$_{0.5}$Fe$_{0.5}$O(111)/Ru(0001) before room temperature C MBE. (c) and (d); Corresponding spectra after annealing to 600 K in UHV.
Prior to C deposition, the AES (figure 4.9a) and EELS spectra (figure 4.9b) are consistent with the XPS data (figure 4.2) indicating a Co/Fe/O atomic ratio of 1:1:2, showing the formation of Co$_{0.5}$Fe$_{0.5}$O(111), with an interband transition near 2.3 eV. C deposition at room temperature followed by annealing in UHV to 600 K indicates the presence of a sp$^2$ C layer (figure 4.9c) with an estimated thickness of 3.2 ML, and with the Co/Fe/O relative intensities unchanged.

EELS spectra (figure 4.9d) indicate the presence of a broad $\pi \rightarrow \pi^*$ feature near 5.7 eV. Thus, annealing the C layer to 600 K in UHV results in a slight decrease in C thickness, but without significant change in oxide composition. Figure 4.10 also shows the C 1s XPS spectra after graphene deposition at room temperature with a C-C peak at about 284.8eV and an additional

![Figure 4.10. The C 1s XPS spectra after graphene MBE on Co$_{0.5}$Fe$_{0.5}$O(111)/Ru(0001) at room temperature.](image)
peak at 287.4 eV indicating the formation of C-O covalent bond formation at room temperature. Corresponding LEED data (figure 4.11) indicate that annealing results in formation of a six-fold LEED pattern with broadened diffraction spots. A detailed analysis (Table 4.1) indicates that the 6-fold LEED prior to deposition displays 6-fold symmetry with an average domain size of ~ 5.5 nm. After annealing of the C layer to 600 K in UHV, the LEED exhibits C\textsubscript{3v} symmetry with similar domain size.

Annealing of the C/Co\textsubscript{0.5}Fe\textsubscript{0.5}O(111) sample to 800 K in UHV resulted in the complete removal of C, and of some lattice O, from the sample.

![Image](image.png)

**Figure 4.11.** The LEED patterns of OH-terminated Co\textsubscript{0.5}Fe\textsubscript{0.5}O(111) before (a) and (b) after C deposition at room temperature and annealing to 600 K in UHV. (Note: after C deposition at room temperature but before annealing, no LEED was visible.) Beam energy was 60 eV.

4.4 Discussion

The data presented above demonstrate that C MBE yields graphene growth on OH-terminated CoO(111) and OH-terminated Co\textsubscript{0.5}Fe\textsubscript{0.5}O(111), and that this growth proceeds by initial formation of a graphene oxide layer with C covalent bonds to the substrate. The observed
behavior for these two hydroxyl-stabilized [27] polar (111) surfaces is similar to that reported for graphene growth on MgO(111), with observation of C-O bond formation within the first C layer, three-fold symmetry in the LEED pattern, and graphene-to-substrate oxide charge transfer [1,4,5]. Thus, the model for graphene/graphene oxide formation reported for Co$_3$O$_4$(111) [22] appears applicable to a range of other polar oxide surfaces—the (111) surfaces of rocksalt-structured oxides.

Breaking the chemical equivalency of the graphene A and B sites leads to a reduction in symmetry from C$_{6v}$ point group to the C$_{3v}$ point group (figure 4.5b, figure 4.11b, Table 4.1) and can lead to a band gap opening at the Dirac point [1], as observed for graphene growth on MgO(111) where a $\sim 0.5 - 1$ eV band gap at room temperature has been reported [1,5]. In the C$_{3v}$ point group, away from the center of the Brillouin zone, there is no mirror plane symmetry in the Brillouin zone line to $K$, the edge of the graphene Brillouin zone, about which the Dirac cone is centered. With the loss of mirror plane symmetry at $K$, the $\pi$ band may not retain pure $p_z$ character, particularly if the graphene does not remain flat in the $x$-$y$ plane as a result of the symmetry reduction. Effectively, for a system that had little spin-orbit coupling, the reduction of symmetry also leads to additional spin orbit coupling. Substrate-induced spin orbit coupling in graphene is known and reported [35]. This “turning on” of spin orbit coupling in graphene has consequences. The spin Hall effect (SHE) in vicinal graphene is generally considered to be practically impossible, because graphene has an extremely small intrinsic spin–orbit (SO) interaction. With a reduction of symmetry to the C$_{3v}$ point group, the added spin orbit coupling now makes spin Hall effect (SHE) possible in graphene [36]. While there is a massive decrease in the spin diffusion length if spin-orbit coupling is turned on, magneto-electric effects, not previously possible, can now occur making graphene much more suitable for spintronic device
applications. Among the effects now expected is an asymmetry of the magneto-resistance in an applied magnetic field. Because the pseudospin states are introduced by the reduction in symmetry, voltage controlled magneto-electric effects may also be possible [37].

In terms of practical applications, the data presented here—particularly the small domain sizes for MBE deposited graphene on CoO(111) and Co_{0.5}Fe_{0.5}O(111) (Table 4.1)—are worthy of note, as such domain walls are a primary cause of spin scattering in graphene [38]. However, much larger domain sizes ~ 2000 Å, have been observed for graphene deposited by MBE on Co_{3}O_{4}(111) [20], so clearly improvement of graphene domain size is possible. The experiments reported here indicate that the CoO(111) and Co_{0.5}Fe_{0.5}O(111) surfaces react with C, resulting in the loss of lattice O for temperatures above ~ 800 K and 600 K, respectively. Therefore, higher deposition/annealing temperatures cannot be used for these systems. However, the ability of H to preferentially etch and remove defect sites in growing graphene layers has been reported, and may be a principal reason for the observed superiority of CVD graphene vs. MBE graphene on h-BN(0001) substrates [16].

4.5 Summary and Conclusions

C MBE yields few layer graphene growth on OH-stabilized CoO(111) and Co_{0.5}Fe_{0.5}O(111) with formation of an intermediate graphene oxide buffer layer. EELS data indicates significant charge transfer from the graphene to the oxides. XPS measurement also indicates the formation of C-O covalent bond formation between the first few graphene layers and the Co_{0.5}Fe_{0.5}O(111). LEED indicates that the graphene/graphene oxide overlayers exhibit C_{3v} symmetry. The results are similar to previously reported results for graphene growth on MgO(111), suggesting a general pattern of graphene/graphene oxide growth on the (111) surfaces rocksalt-structured oxides. The observation of C_{3v} for the graphene/graphene oxide
overlayers indicates that band gaps and enhanced spin orbit coupling should be observed in these systems. The data therefore indicate that graphene growth on rock-salt structured oxide (111) surfaces should exhibit enhanced spin orbit coupling, a spin Hall effect and band gaps—with significant implications for spintronic device applications.

4.6 Funding

Work at UNT was supported by NSF under grant no. ECCS-1508991, by C-SPIN, a funded center of STARnet, a Semiconductor Research Corporation (SRC) program sponsored by MARCO and DARPA under task IDs 2381.001 and 2381.006, and by the STARnet undergraduate summer internship program.

4.7 References


CHAPTER 5

DIRECT MBE GROWTH OF GRAPHENE ON THICK Co$_3$O$_4$(111)/Ru(0001) SURFACE$^3$

5.1 Introduction

Graphene is a one atom thick layer of C atoms arranged in a honeycomb lattice (figure 1) and has attracted a lot of interest in both electronics and spintronics, due to its high carrier mobility, quantum hall effect, long carrier mean free path, long spin diffusion length, spin induced polarization when in proximity to a magnetic substrate, high thermal stability and high specific area [1–9].

Figure 5.1. The Atomic structure of graphene [7].

The direct growth of monolayer and multi-layer graphene onto a magnetic, insulating substrate by industrial scalable methods is technologically important for graphene-based devices for spintronic application. This is because of experiments indicating that interfacial spin-spin interactions can spin polarize graphene charge carriers, without the necessity for inefficient spin injection [6,10,11]. However, the currently popular method involves the peeling off of graphene

$^3$ Work reported in this chapter was done in collaboration with Dr. Peter Dowben Group (University of Nebraska, Lincoln).
from HOPG or the growth of graphene on a metallic substrate followed by physical transfer to a dielectric substrate [12–14]. This method is not scalable, causes azimuthal misalignment of the heterostructure and also introduces contamination to the film.

Previous studies have reported layer-by-layer growth of azimuthally oriented graphene on a 10 Å thick Co$_3$O$_4$(111)/Co(0001) film, with substrate-induced spin polarization of the graphene layer [11,15]. This strongly suggests a route towards graphene-based spintronics without the necessity for the injection of spins into the graphene, which tends to be inefficient [6,10]. Theory also indicates that the growth of graphene on certain incommensurate substrates such as Co$_3$O$_4$ (111) occurs with substantial graphene-to-oxide charge transfer due to C-oxide covalent bond formation [16]. The result is an interfacial graphene oxide buffer layer on top of which occurs subsequent layer-by-layer growth of azimuthally aligned graphene.

Although previous studies have shown graphene deposition on 10 Å thick Co$_3$O$_4$(111)/Co(0001) [15], typical device requirements, for example, a non-local spin valve [6], require an oxide sufficiently thick to inhibit the tunneling between the substrate and the graphene to prevent shorting. The focus here, therefore, is on the growth of graphene on Co$_3$O$_4$(111) layers thick enough for non-tunneling device applications. Studies of graphene deposition were carried out on a 250Å Co$_3$O$_4$(111)/Ru(0001)/Al$_2$O$_3$(0001) by MBE to confirm the theoretical predictions regarding formation of interfacial graphene oxide, and to yield device-worthy heterostructures. AES, LEED, EELS and XPS indicated the successful growth of Co$_3$O$_4$(111) on Ru(0001) and subsequent growth of graphene on the Co$_3$O$_4$ (111). LEED studies showed a reduction in graphene symmetry from C$_{6v}$ to C$_{3v}$ symmetry. XPS showed that the Co$_3$O$_4$(111) surface region was reduced to the +2 oxidation state (CoO) and EELS showed a prominent $\pi$ to $\pi^*$ transition peak showing a significant charge transfer from the C to the oxide layer. The C 1s
XPS spectra also confirms the formation of the C-O covalent bond formation, and the formation of a graphene oxide overlayer. These results indicate that interfacial charge transfer from the graphene to the cobalt oxide layer is a major factor in graphene oxide formation and subsequent graphene growth on an incommensurate substrate and might be important for applications in spintronics.

5.2 Experimental

The Ru(0001) film used in this experiment was fabricated on a Al₂O₃(0001) substrate in a separate chamber and then transferred to the MBE/analysis chamber used for both Co₃O₄(111) and graphene growth, as described in chapter 2. The Co₃O₄(111) and the graphene growth were then performed on the cleaned Ru(0001) as described in chapter 3 and 4 respectively. Auger, XPS, EELS and LEED were performed to characterize the sample surface. Typical Auger and LEED spectra of a clean Al₂O₃(0001) substrate used in this work are shown in figure 5.2 and 5.3.

![Figure 5.2. The Auger electron spectra of clean Al₂O₃ (0001)](image)
5.3 Results and Discussion

Figure 5.2 shows the Auger spectra of the clean alumina substrate obtained after annealing at 1000K in 1 x 10^-7 Torr O₂ followed by in UHV. The corresponding LEED images of the clean alumina at different electron energies are shown in figure 5.3. Auger of Al₂O₃(0001) show the Al (LVV) line shape at low energy and the O (KVV) line. The presence of only Al and O auger peaks and absence of C peak confirms that the Al₂O₃(0001) substrate is clean and devoid of any contamination.

![Image](image.png)

**Figure 5.3.** The LEED images of clean Alumina at different energies. (a) 100eV; (b) 180eV; (c) 250eV.

The LEED of the Al₂O₃(0001) substrate showed the typical three-fold pattern expected for the Al₂O₃(0001) surface [17,18]. The sharp diffraction beams in the LEED patterns over a range of energies indicates that the Al₂O₃(0001) substrate is highly ordered, as expected for a single crystal. Figure 5.4a shows the characteristic hexagonal LEED image obtained after the deposition of Ru(0001) on Al₂O₃(0001) followed by subsequent anneal at 1000 K. After deposition of about 250Å of Co₃O₄(111) on the Ru(0001) surface, the LEED showed a six-fold LEED pattern with the presence of twinning. This aligns with the results reported in the literature [18]. Reports show that Co₃O₄(111) grown on substrates such as Ru(0001), Al₂O₃(0001) and Ir
display hexagonal LEED patterns with extra spots in between the main hexagonal LEED pattern, indicating presence of twinning [18–21].

The XPS data in figure 5.5a shows that before C deposition and annealing, the Co 2p spectrum is representative of Co$_3$O$_4$(111) with a suppressed shake-up peak at 788.8eV and a Co 2p$_{3/2}$ peak at 779.8eV containing both Co$^{2+}$ and Co$^{3+}$ as described in chapter 3 [18,20,22]. After deposition and anneal at 800K in UHV, the Co 2p spectrum (figure 5.5b) is sharply different and representative of Co$^{2+}$ as in CoO with a broadened feature at 780.1eV and a prominent shake-up feature at 785.2eV [22,23]. Another distinctive difference between these peaks is the Co2p$_{1/2}$ shake-up peaks which are at 804eV for Co$_3$O$_4$(111) and 802 eV for CoO(111), as described in chapter 3[22]. The emergence of a large shake-up feature at 802 eV after C deposition and annealing (figure 5.5b) is further evidence of oxide reduction to the CoO phase. Such a reduction is consistent with previous results on nanotrin films which shows the reduction in total oxide thickness from 10Å to ~7Å [16]. Furthermore, more additional experiments (not shown here) indicate that further annealing at 800K and higher temperature, can result in the complete loss of

![Figure 5.4](image_url). The LEED images of (a) clean Ru(0001); (b) Co$_3$O$_4$(0001)/Al$_2$O$_3$(0001) LEED images were acquired at 60eV.
C and lattice oxygen. Thermodynamics data strongly suggest that this is due to the following reactions at 800 K and CO pressure of $10^{-8}$ Torr [24].

\[
C(s) + Co_3O_4(s) \rightarrow CO(g) + 3CoO(s), \quad \Delta G_{\text{reaction}} = -195.86 \text{KJ/mol}
\]

\[
C(s) + CoO(s) \rightarrow CO(g) + Co(s), \quad \Delta G_{\text{reaction}} = -115.218 \text{KJ/mol}
\]

Figure 5.5. The Co(2p) XPS spectra of Co$_3$O$_4$(111)/Ru(0001). (a) before C MBE (b) after C MBE at 800K and anneal at 800K.

XPS of the C 1s spectra after C deposition and anneal at 800K is shown in figure 5.6a with the O 1s spectra of Co$_3$O$_4$(111) before and after C MBE and anneal at 800K shown in figure 5.6b. The 2.7ML C 1s XPS spectra obtained after anneal show a peak at 285.3eV binding energy which depicts graphene-to-oxide charge transfer is confined to the first few monolayers of C.

Figure 5.6. The (a) C 1s XPS spectra after C MBE at 800K and anneal at 800K. (b) O 1s XPS spectra of Co$_3$O$_4$ (I) before C MBE; (II) after C MBE and anneal at 800K.
O 1s spectra shows that the film is OH-stabilized before and after C MBE. Figure 5.7 shows the Auger spectrum of ~250Å Co₃O₄(111) deposited on Ru(0001) before and after C deposition and anneal at 800K while figure 5.8 shows the LEED data after C MBE and anneal. Figure 5.7b shows a C(KVV) lineshape that is indicative of an sp² C which is absent in figure 5.7a [25]. After C MBE and anneal, a diffuse, hexagonal LEED pattern was obtained characteristic of hexagonal graphene, albeit with small domain size of 3.5nm as shown in table 5.1 [26]. However, there is a reduction in the symmetry to C₃ᵥ as shown in table 5.1. The breaking of symmetry from C₆ᵥ point group to C₃ᵥ point group was also observed in chapter 4 when graphene was grown directly on CoO(111) and Co₀.₅Fe₀.₅O(111) surfaces. This observation indicates the presence of spin-orbit coupling in the graphene layer on oxide with implication of band gap opening and room temperature spin Hall effect (SHE) [27–30].

![Figure 5.7. The Auger electron spectra of (a) ~250Å Co₃O₄ (b) C MBE on Co₃O₄ (111) at 800K followed by annealing in UHV at 800K.](image)

After C MBE at 800K but before anneal, the XPS C 1s estimated thickness was ~3ML with no LEED pattern but after anneal at 800K in UHV, the XPS estimated thickness was 2.7ML with the appearance of a long range order in the graphene overlayer. This confirms an ordered graphene layer was formed [13,15].
Figure 5.9 shows the EELS spectra obtained at a electron primary energy of 100eV before and after C MBE and anneal in reflection mode. A beam energy of 100 eV is required to be able to probe the very few monolayers of the film in the surface region. Figure 5.9a shows characteristic EELS spectra for Co₃O₄(111) film with peak at about 2.1eV extending to about 3.0eV and a peak at about 7.5eV indicative of the interband transition peak as established in chapter 3 [31–33]. This EELS data confirms the formation of Co₃O₄(111). Figure 5.9b shows the EELS spectra obtained after C MBE at 800 K and after anneal at same temperature. The EELS data show the disappearance of the interband transition peaks of the Co₃O₄(111), but also showed the appearance of the π to π* transition peak at 5.7 eV with substantial charge transfer.

Table 5.1. LEED intensity and domain analyses for C on Co3O4(111) surface. LEED was acquired at 60eV beam energy. LEED domain sizes and symmetry determination was carried out by Dr. Dowben’s group at the University of Nebraska, Lincoln.
This is consistent with previous ellipsometry measurements [15]. The absence of an observable cobalt oxide interband transition or surface plasmon peak is indicative of a continuous film and the surface sensitive nature of a 100eV electron primary beam energy with inelastic mean free path of about 7 Å through carbon [34]. This confirms that the loss peaks of the 2-3 ML of the graphene layer was observed. However, this value is in contrast to the 5 eV energy observed for unsupported graphene [35,36]. Therefore, the EELS spectra in figure 5.9b indicate charge transfer to the oxide substrate and corroborates the theoretical findings [16].

5.4 Summary, Conclusion and Future Prospects

LEED, AES, XPS and EELS spectroscopy were used to characterize the growth of 250 Å thick Co₃O₄ (111) on Ru(0001) and subsequent graphene growth on the oxide by MBE using graphite rod source. XPS, EELS and LEED confirms the formation of Co₃O₄(111). XPS demonstrates the formation of a C-O bonding and also a reduction of Co from the +3 to +2 states within the oxide surface region. The EELS data indicate a significant graphene-to-oxide charge transfer in excellent agreement with predictions. LEED result indicates that graphene grown on
this oxide exhibit $C_{3v}$ symmetry which can lead to band gap formation and room temperature spin Hall effect. These results therefore, suggests that this model can be extended to other p-type magnetic oxides with high magnetic ordering temperature for applications in spintronics and graphene based devices.

However, for these devices involving graphene on the different cobalt oxide phases and Iron oxides, there is a narrow temperature and time window at which they are stable. The results obtained in this work suggests that annealing the graphene/cobalt oxide heterostructures at higher temperatures and longer times result in the loss of both C and lattice oxygen. The thermodynamics calculation shown in table 5.2 explains why the reaction of coking is thermodynamically feasible.

<table>
<thead>
<tr>
<th>Rock salt oxides</th>
<th>$\Delta G_{\text{reaction}}$ of $\text{M-O}_2(\text{s}) + \text{C}_2(\text{s}) \rightarrow \text{M}(\text{s}) + \text{CO}_2(\text{g})$ (KJ/mol)</th>
<th>In-plane $\text{O}^{2-}$—$\text{O}^{2-}$ lattice constant (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO(111)</td>
<td>+237.082</td>
<td>2.97</td>
</tr>
<tr>
<td>CoO(111)</td>
<td>-115.218</td>
<td>3.02</td>
</tr>
<tr>
<td>FeO(111)</td>
<td>-84.588</td>
<td>2.90</td>
</tr>
<tr>
<td><strong>Spinel oxide</strong></td>
<td>$\Delta G_{\text{reaction}}$ of $X_3\text{O}_4(\text{s}) + \text{C}_2(\text{s}) \rightarrow 3\text{XO}_2(\text{s}) + \text{CO}_2(\text{g})$ (KJ/mol)</td>
<td></td>
</tr>
<tr>
<td>Co$_3$O$_4$(111)</td>
<td>-195.86</td>
<td>2.85</td>
</tr>
</tbody>
</table>

Table 5.2. The in-plane $\text{O}^{2-}$—$\text{O}^{2-}$ lattice constant for oxides and their $\Delta G_{\text{reaction}}$ for coking in vacuum. Temperature of reaction=800K; partial pressure of CO=10$^{-8}$ Torr. $\Delta G$ values were obtained from the Handbook of chemistry and physics [24].

for CoO, Co$_3$O$_4$ and FeO but not MgO under vacuum. This indicates that higher annealing temperatures usually correlated with good and high quality graphene cannot be used on these substrates [13]. On the other hand, graphene growth on MgO has been demonstrated and also
Graphene growth on MgO(111) can be carried out at higher temperatures. This therefore suggests that the direct growth of graphene on cobalt oxides might work if one is satisfied with small domain graphene which may be allowable for spin Hall devices [37], but that applications requiring larger domains (less domain wall scattering) would require an MgO(111) substrate. In this regard, it is notable that graphene platelets have been formed on MgO(100) by chemical vapor deposition at temperatures > 1000 K with no evidence of substrate reaction [38].

Hence, the ability to fabricate an heterostructure of graphene/CoO(111)/Ru(0001), graphene/Co_{0.5}Fe_{0.5}O(111)/Ru(0001) and graphene/Co_3O_4(111)/Ru(0001) by MBE at not more than 800K processing temperature is a significant step towards making a graphene spin-based device which explores the property of spin induced polarization of the graphene electrons when in proximity to a magnetic oxide rather than spin injection leading to non-volatile and high processing speed device.

5.5 Funding

This work was supported by the NSF under grant no. ECCS-1508991

5.6 References


