Area Selective Deposition of Ultrathin Magnetic Cobalt Films via Atomic Layer Deposition

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Abstract
The work investigates the selective deposition of cobalt oxide via atomic layer deposition. Methoxysilanes chlorosilane and poly(trimethylsilylstyrene) self-assembled monolayers are utilized to prevent wetting of water and cobalt bis(N-tert butyl, N'-ethylpropionamidinate) from the substrate, thereby controlling nucleation on the substrate and providing a pathway to enable selective deposition of cobalt oxide. Sr and Al are deposited atop the oxide films to scavenge oxygen and yield carbon-free cobalt metal films. Thermal reduction of the oxide layer in the presence of CO and H$_2$ was also investigated as an alternative. Finally, we demonstrate control over the tunability of the coercivity of the resultant films by controlling the reduction conditions.

1. Introduction
Ferromagnetic thin films find applications in a variety of fields, such as electronics, spintronics, RF technology, energy, etc. With ever-decreasing feature sizes of the devices required, film conformity and crystalline structure become very important to determining magnetic properties. As such, atomic layer deposition (ALD) is a very attractive technique for magnetic film deposition as it ensures atomic level conformity. Since ALD film growth necessarily involves a film nucleation step, it is possible to engineer the surface energy of the substrate to cause preferential wetting and nucleation in only desired areas, resulting in area selective ALD (AS-ALD). Unlike conventional photolithography-based fabrication, such a bottom-up patterning approach could eliminate the need for subsequent etch steps, reducing the cost of fabrication and overcoming scaling limitations in manufacturing devices. This work investigates the selective deposition of cobalt metal via AS-ALD for use as the free magnetic layer within the magnetic tunnel junction of spin-transfer torque random access memory.

2. Experimental
Figure 1 depicts the experimental setup used to perform the work herein. This setup allows for the in-situ x-ray photoelectron spectroscopy (XPS) to determine film stoichiometry and atomic oxidation states. Direct reduction of cobalt organometallic precursors can lead to the incorporation of carbon and other ligand constituents into the film, as shown in Figure 2. In order to achieve a high degree of purity, cobalt was first deposited as cobalt (II) oxide at 180 °C using cobalt bis(N-tert butyl, N'-ethylpropionamidinate) and water as the co-reactant. Reflection high energy electron diffraction and x-ray diffraction are used to determine film crystallinity and structure of CoO and Co. While the CoO thin films grown on amorphous thermal oxide SiO$_2$ vary from amorphous to polycrystalline, the CoO thin films grown on single crystal substrate MgO(100) are crystalline and epitaxial. The resultant films were then subsequently reduced ex-situ to yield cobalt metal using several approaches.

3. Results and Conclusions
3.1 Deposition
We explore the use of the self-assembled monolayer (SAM) n-octadecyl(dimethylchlorosilane) (ODTS) as a means to selectively inhibit the surface nucleation of CoO on SiO$_2$, HfO$_2$ and MgO substrates. Preliminary results are depicted in Figure 3. ODTS successfully blocks the deposition of 6 nm of CoO on HfO$_2$. We have also investigated the blocking capabilities of methoxysilanes and poly(trimethylsilylstyrene).

3.2 Reduction
We demonstrate the reduction of CoO to form carbon-free Co metal using two methods: (i) Utilizing a layer of aluminum or strontium to scavenge oxygen and (ii) thermally reducing CoO in the presence of carbon monoxide or hydrogen gas. As shown in Figure 4, a 30 min anneal at 420 °C in the presence of 0.111 mbar of carbon monoxide resulted in the complete conversion of the oxide film to Co metal. We also demonstrated that reduction in CO is possible at temperatures as low as 350 °C. Similarly, we have also demonstrated the use of hydrogen in the reduction.

Figure 5 shows the XPS spectra of a 4.5 nm CoO film capped with a 3nm Sr layer. The Sr acts as an oxygen sink, and, upon annealing at 450 °C, converts the entire oxide film therewith to cobalt metal. We have also demonstrated the use of aluminum as an oxygen sink for the same purpose.

A superconducting quantum interference device (SQUID) was utilized to measure the coercivity of the cobalt layer, as depicted in Figure 6. It has been shown therewith that the reduction conditions affect the structure of the resultant film.
affecting the magnetic properties as well; hence demonstrating control of the film’s coercivity over a wide range.

4. Summary
Within this work, we investigate the area selective deposition of cobalt metal. We deposit cobalt (II) oxide via ALD to ensure contaminant free films, utilizing methoxysilanes, chlorosilanes and poly(trimethylsilyl)styrrene as blocking layers to facilitate selective deposition. We demonstrate that the aforementioned SAMs are capable of preventing CoO deposition up to 350 ALD cycles (corresponding to 10 nm). Then, we show the ability to reduce the oxide film both by using a reducing gas as well as by depositing and oxygen scavenging layer. For the first time, we illustrate a path to selectively deposit ultrathin magnetic cobalt films. Finally, we explore the dependency of film coercivity with the reduction conditions.

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References
Fig. 4 Reduction of CoO to Co by annealing at 420 °C under 0.111 mbar of CO.

Fig. 3: 200 cycles (6nm) of CoO on HfO$_2$ without (top) and with (bottom) of a blocking monolayer of n-octadecyldimethylchlorosilane.

Fig. 5 Reduction of a 4.5 nm CoO film by depositing 3 nm Sr and a 30 min vacuum anneal at 450 °C.

Fig. 6 SQUID measurements of SrO/Co/MgO(001) (blue color), and SrO/Co/CoO/MgO(001) (red color) heterostructures as a function of applied magnetic field measured at 300 K.