

Fingerprinting Chemistry and Magnetism at the Nanoscale using SX-STM

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Abstract

The emerging technique of synchrotron x-ray scanning tunneling microscopy (SX-STM) has shown promise for gaining a better understanding of the structure, chemistry, and magnetic properties of nanoscale materials on surfaces. Currently, the Advanced Photon Source constructs a dedicated beamline for the world's first user program in SX-STM. We worked with Volker Rose with the goal of ultimately shrinking the physical space that magnetic domains occupy in order to minimize space without limiting data storage capacity.

Background

Scanning Tunneling Microscope (STM)

The scanning tunneling microscope has been utilized since the 1980's to measure the topography and determine the elemental identity of the top layer of a sample. This technique uses a very fine tip that moves just above the surface of a sample. At this time, *outermost electrons* tunnel their way through empty space to the tip of the STM. This data creates the topography image.

Synchrotron X-rays (SX)

The principles of the synchrotron can be dated back to the 1940's. Since then, x-rays emitted from the synchrotrons have been used in a variety of experiments, primarily for x-ray diffraction and x-ray fluorescence. For example, Rosalind Franklin used x-ray diffraction while studying DNA fibers. One of her photographs (Figure 1) provided vital insights into the DNA structure, which other scientists used to support the double-helix shape. Synchrotron x-rays can also be used to determine the elemental identity of a substance with a method called x-ray fluorescence. This method bombards a sample with x-rays causing atoms' *inner core* electrons to be ejected from the sample. As other electrons fall into that now vacant orbital, energy is given off in the form of light. That light is detected, energies are calculated, and then matched to energy values of known elements.

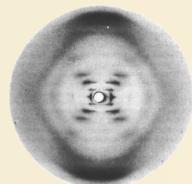


Figure 1: Image 51; Rosalind Franklin's x-ray diffraction of DNA Source: CE&N news

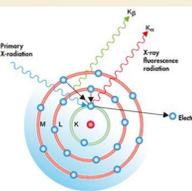


Figure 2: Atomic model x-ray fluorescence depiction Source: Fischer Technology Inc.

Experimental Technique

Synchrotron X-ray Scanning Tunneling Microscopy (SX-STM)

Dr. Volker Rose has paired scanning tunneling microscopy with synchrotron x-rays, which utilizes the strengths of each instrument to deliver a more accurate verification and location of elemental identity with a topographic scan. One main way that Dr. Rose's instrument is functionally different than a STM is that x-rays are used to excite inner core electrons from the sample, causing them to "float" outside of their atom's pull and tunnel to a sharp tip of the SX-STM. Similar to an STM, this tip is connected to a monitor measuring current, but instead of only the outermost electrons being detected, the inner core electrons (that were excited by the x-rays) also contribute to the current recorded. Through a distinction between the two types of electrons (inner core and outer core) tunneling to the tip, the amount, or relative intensity, of inner core electrons that tunneled are linked to the energy of the x-ray that caused them to be excited to the top. A SX-STM intensity vs energy spectrum is created and the peaks are then matched to the known binding energies of electrons of specific elements. This verifies the elemental identity of the atom while also specifying the exact location of that atom.

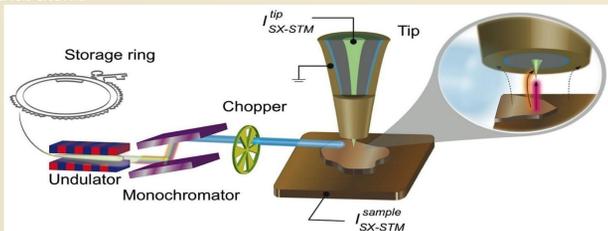


Figure 3: Schematic of the SX-STM instrument designed by Dr. Volker Rose.

Experimental Conditions and Method

Sample Choice

We chose to deposit cobalt on a copper surface due to their chemical and physical properties. Cobalt is ferromagnetic at room temperature; its magnetic properties are due to the unpaired electrons in the 3d orbitals (Figure 4). Copper was chosen as the substrate because copper is relatively easy to clean. A photo of the copper substrate is shown in Figure 5, to the right.



Figure 4: Abbreviated electron configuration of Co. Three unpaired electrons in the 3d orbitals cause the magnetic properties of cobalt. Figure 5: Copper sample

Sample Preparation

Before creating the nano islands of cobalt on the copper surface, the copper sample was first placed into the preparation chamber (Figure 6) to be cleaned. Although to the naked eye, the copper sample might look clean, a thin oxide layer has likely formed on the exposed copper surface due to the oxygen in our atmosphere. We cleaned the surface by sputtering it with argon ions which displace the oxides or other impurities. This process was done at room temperature and at a low pressure of about $\sim 10^{-6}$ torr. Because the sputtering process consequently damages the surface, the sample was then annealed, which smooths out the pure copper surface. The temperature and pressure conditions for annealing were 700 K and $\sim 10^{-10}$ torr. To confirm that the sputtering process cleaned the copper of all impurities, Auger electron spectroscopy was performed and the results are shown to the right (Figure 7). Now that the substrate was clean, it was ready for the depositing of cobalt nano islands.

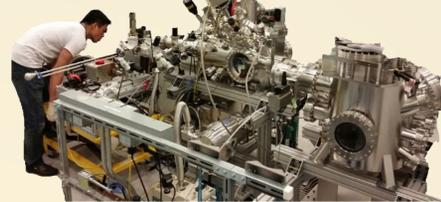


Figure 6: Sample preparation chamber

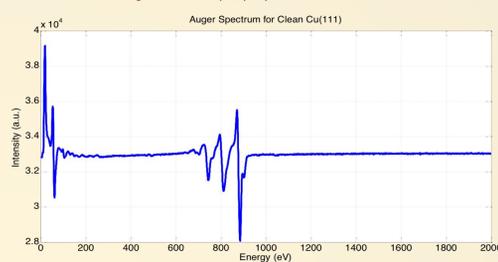


Figure 7: Auger electron spectrum (AES) obtained in the preparation chamber for the Cu(111) surface after cleaning.

To do this, the solid cobalt rod sitting above the sample inside the preparation chamber was heated to a temperature of 1500°C, while still keeping the pressure around $\sim 10^{-6}$ torr, for a duration of 30 seconds. At this temperature and pressure, the solid cobalt sublimed into its gas phase, where cobalt particles then attached to the copper substrate in a "nano island" fashion as shown to the right (Figure 8). Auger electron spectroscopy was performed to confirm that the cobalt was in fact deposited onto the copper, and also to check that there were no impurities such as oxides, nitrides, or carbides that formed during the sample preparation process. The Auger electron spectrum to the right (Figure 9) shows peaks at 656 eV and 716 eV which are characteristic of cobalt and peaks at 750 eV, 810 eV, and 890 eV which are characteristic of copper. A small peak around 510 eV represents oxygen, which signifies that a small amount of copper oxide formed during sample preparation. Due to time constraints, and the small size of the oxygen impurity, the sample was still used.

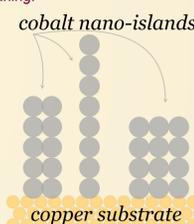


Figure 8: Side view representation of copper substrate with cobalt.

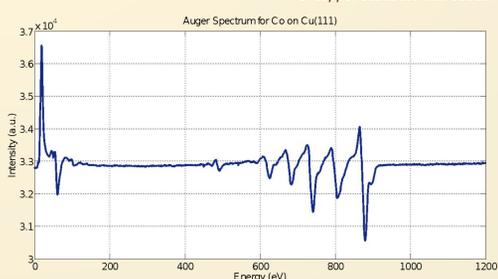


Figure 9: Auger electron spectrum (AES) obtained in the preparation chamber after the deposition of Co islands on Cu(111) surface.

Vacuum Suitcase

To ensure that the sample remains uncontaminated, a vacuum suitcase (Figure 10) is used to transport the sample from the preparation chamber to the SX-STM, which is located at the Advanced Photon Source. This vacuum suitcase has a pressure around $\sim 10^{-11}$ torr, which is the same as the sample preparation chamber. The suitcase is then attached to the SX-STM to transfer our sample without exposing it to the atmosphere.

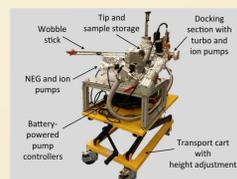


Figure 10: Vacuum suitcase used for transport.

Beamline, SX-STM

The sample was then removed from the vacuum suitcase and placed into the SX-STM instrument. Figure 11 shows a picture of the instrument at the Advanced Photon Source x-ray beamline and Figure 3 is the schematic of the SX-STM instrument. Liquid nitrogen was used to cool the SX-STM to a temperature of 150 K, additionally the instrument was kept at a pressure of $\sim 10^{-11}$ torr.

After the above conditions were achieved, the sample placement was completed, and then the scanning tunneling microscope tip was aligned to the sample. The SX-STM was set to a scan range of 100 nm by 100 nm on the sample. A bias voltage of -1 volts and a current of 1 nanoampere were used. The x-ray photon energy was ramped between 760 and 800 eV for the SX-STM spectroscopy recordings.

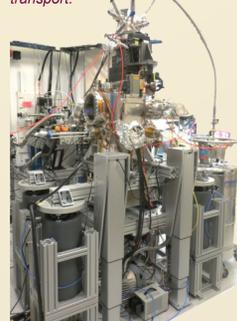


Figure 11: SX-STM at the APS beamline.

Results

Figure 12 shows the topographic view of the sample analyzed using the SX-STM. Since the intensity vs energy graphs were recorded in relation to the position of the SX-STM tip on the sample, each graph gives us extreme accuracy in the identity and location of the element. Figure 13 shows the graph during the tip location on a cobalt nano island, and Figure 14 shows the values/identities of the characteristic peaks.

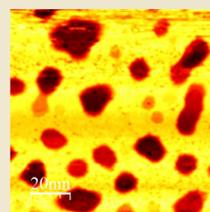


Figure 12: SX-STM topography of cobalt nano islands on Cu(111)

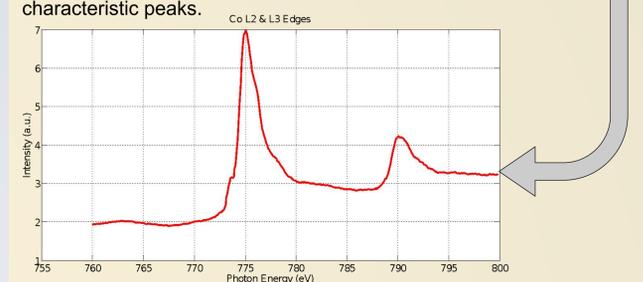


Figure 14 (right): Electron binding energies, in electron volts, for select elements in their natural forms. Source: <http://xdb.lbl.gov/>

Element	K Is	L ₁ 2s	L ₂ 2p _{1/2}	L ₃ 2p _{3/2}	M ₁ 3s
23 V	5465	626.7†	519.8†	512.1†	66.3†
24 Cr	5989	696.0†	583.8†	574.1†	74.1†
25 Mn	6539	769.1†	649.9†	638.7†	82.3†
26 Fe	7112	844.6†	719.9†	706.8†	91.3†
27 Co	7709	925.1†	793.2†	778.1†	101.0†
28 Ni	8333	1008.6†	870.0†	852.7†	110.8†
29 Cu	8979	1096.7†	952.3†	932.7†	122.5†
30 Zn	9659	1196.2*	1044.9*	1021.8*	139.8*

Further Applications

SX-STM is a method that would allow for the verification of virtually any sample's *elemental identity* within *sub-nanometer spatial resolution*. While this is a technique that can have many applications, further investigation of our cobalt nano island samples with the SX-STM could reveal the magnetic domains that the cobalt nano islands possess. This research can be applied to the creation of smaller hard drives with the ability to store the same amount of data in a much smaller physical space as compared to today's current hardware. Figure 15 shows a representation of how magnetic domains are possibly arranged in a hard drive, along with how the change in magnetic domain directions translate into binary 1's and 0's. Figure 16 shows how the magnetic domains of the nano islands of a sample can be arranged to convey this same message while using only nanometers of space.



Figure 15: Representation of alternating magnetic domains, the foundation for hard drive data storage. The alternating directions of the magnetic domains would translate into 1's and 0's for data storage.

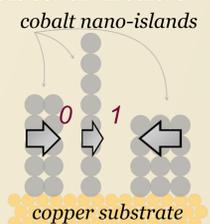


Figure 16: Side view representation of copper substrate with cobalt nano islands, and the domains that they could theoretically possess and therefore translate to recorded data.

Acknowledgements

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