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				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of California, San Diego Dept. Of Chem & Biochem 9500 Gilman Dr. La Jolla, CA 92093--358				8. PERFORMING ORGANIZATION REPORT NUMBER	
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1. COVER SHEET: FINAL REPORT ON AFOSR DURIP GRANT

PIs: ANDREW KUMMEL:

Title: "Instrumentation for Deposition and Etching of Ferromagnetic Nanoparticles"

Grant#: F49620-99-1-0115

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1.5 ABSTRACT:

During this award, accomplishments were made in three areas: deposition of anisotropic ferromagnetic nanoparticles, etching of metallic materials, and oxidation of metals. (a) The grantees developed a technique to deposit partially anisotropic Fe nanoparticles, $200 \text{ \AA} \times 70 \text{ \AA} \times 8 \text{ \AA}$ on Ag(111) with a uniform directionality. The investigators also found that in UHV, the silver atoms spontaneously diffuse on top of the Fe nanoparticles even at 300 K. Since silver is much more difficult to etch than iron due to the lack of volatile silver halides, this spontaneous coating of Fe by Ag explains the difficulty in etching Fe particles deposited on Ag substrates. (b) The grantees also investigated the basic mechanisms of etching of Al(111) by a halogen gas, ICl. Halogen etching of metallic materials is a critical step in fabrication of magnetic sensors, spin valves, and giant magneto resistive sensors. They found that for ICl/Al(111) the primary chemisorption process is remote dissociation in which the substrate harpoons in incoming ICl molecule with an electron. The dominant chemisorption process is abstraction in which ICl deposits the iodine atom onto the surface while the chlorine is ejected back into the gas phase. (c) The grantees investigated the oxidation of Al(111) by O_2 and NO. Al(111) was chosen since adsorbates do not diffuse on this surface at 300 K so the chemical dynamics can be investigated with room temperature STM. In both cases, it was found that chemisorption occurs via non-adiabatic charge transfer from the surface and results in abstractive chemisorption: one of the atoms from diatomic molecule sticks to the surface while the remaining atom is ejected back into the gas phase. In the case of NO, the reaction is chemically selective: the oxygen sticks to the surface while the nitrogen is ejected back into the gas phase.

2. OBJECTIVES:

Our original goal was to study the two-stage growth of ferromagnetic nanoparticles on a nonmagnetic substrate. We have redirected our focus to study the etching of materials used in giant magnetoresistance devices in order to work collaboratively with the nanomaterials MURI at the Univ. of Florida.

3. STATUS OF EFFORT:

Several critical milestones have been passed. (1) The 4 rod electron beam evaporator has been installed in our scanning tunneling microscopy (STM) chamber. (2) Clean Ag(111) substrate has been prepared and examined with STM and Auger electron spectroscopy. (3) Fe nanoparticles have been deposited on the Ag(111) substrates and examined with STM and Auger electron spectroscopy. (4) Arrays of spatially anisotropic Fe nanoparticles, $200 \text{ \AA} \times 70 \text{ \AA} \times 8 \text{ \AA}$ have been grown on Ag(111) with a uniform directionality. (5) Very preliminary data suggests that the small Fe nanoparticles are at least partially covered with Ag atoms which would explain why they are difficult to etch. (6) The quadrupole purchase with the DURIP funds has been installed. The ionizer is a bit slower than expected so the vendor is working to fix this problem. (7) We have completed a detailed study of halogen chemisorption and etching on aluminum, a low work function metal. (8) We have completed a detailed study of O_2 and NO oxidation on aluminum, a low work function metal.

4. ACCOMPLISHMENT/NEW FINDINGS:

Upon receipt of our DURIP grant, we ordered a Hidden quadrupole mass spectrometer for use in the etching studies. The quadrupole had a large insertion depth (28") so it could intercept the scattered flux from the sample during etching experiments. We also wanted the quadrupole to have fast time response so that we could determine the translation energy of the etch products. Unfortunately, the ionizer is slow; the time response is about 1 msec instead of 10 microseconds. This is due to the

filaments being parallel to the axis of the quadrupole. The vendor is design a new fast ionizer for us to correct this problem using a proven design from the Cosma and Kern groups. In the meantime, we have been using our experimental equipment to study magnetic particles deposition and etching and oxidation of materials used in magnetic devices.

Our initial goal is to deposit isotropic and anisotropic NiFe nanoparticles on a Ag(111) substrate. Co-deposition of NiFe and Ag should prevent coalescence. Normal incidence deposition will be employed to grow disk shaped islands while glancing incidence deposition will be used to grow elongated islands. Recent work by Polsema has show that glancing incidence deposition forms elongated islands even for submonolayer deposition.

We started our metal studies by preparing clean, flat Ag(111) surfaces which are suitable for Fe nanoparticle deposition. Typical single crystal metal surface cleaning procedures involve repetitive sputter-annealing cycles. However, for soft metals such as silver, annealing often results in step bunching and thus small terrace widths. For Ag(111), we found that short cycles of Ar⁺ sputtering along 300 C annealing quickly roughened our crystals. We adjusted the cleaning procedure to reduce the thermal cycling by lengthening both the sputter times and raising the annealing temperature. We now can consistently prepare beautiful clean surfaces which are readily examined with STM (scanning tunneling microscopy). The Ag(111) terrace widths are routinely 100-500 angstroms, and larger terraces can be found by searching with the STM.

We calibrated the iron flux using a quartz crystal microbalance. Afterwards, we deposited a low coverage of iron nanoparticles on the Ag(111) surface. We were able to image the nanoparticles using STM. The particles had diameters of 10-30 angstroms and were 1-3 monolayers tall. We are now learning how to control the growth conditions to make larger particles. The smallest particles do not diffuse at 300 K, but they have a non-polygonal structure which suggests either silver incorporation or diffusion within the particles. The larger iron particles have a pentagonal shape which we would expect for pure iron particles on the Ag(111) substrate.

By increasing the deposition time, we first saturate the step edges with iron particles and subsequently form spatially anisotropic particles on the Ag terraces. These anisotropic particles are approximate 200 Å long and 70Å wide with a height of 6 Å. We do not know the cause of the spatial anisotropy; however since the long axes are always perpendicular to the step edges, we suspect the anisotropy is related to transmission of stress through the Ag(111) substrate.

We plan to use the Fe/Ag(111) nanoparticles to study the etching of Fe nanoparticles by halogens and CO. We want to investigate the chemical selectivity of halogens for Fe versus Ag and the effects of cluster size on chemical reactivity and etching. Preliminary studies indicate that the Fe nanoparticles on silver may be covered with a monolayer of silver atoms. This would explain why even etching with carbon monoxide is slow and requires ion stimulation. The evaporator was sent back to Oxford for repairs since it was never able to provide a constant deposition rate. The repairs took almost 12 months. In the meantime we studied halogen etching of single metallic crystals since this did not require an evaporator

The interaction of ICl and Al(111) involves remote dissociation in its chemisorption process. We have determined that ICl can chemisorb onto Al(111) by non-activated direct chemisorption, and the sticking probability of this direct channel is 0.65 +/- 0.03. Furthermore, low energy ICl molecules that do not undergo remote dissociation can chemisorb onto Al(111) by precursor-mediated chemisorption. Not only is the interaction of ICl and Al(111) reactive, it is chemically selective. Auger spectroscopy and time-of-flight (TOF) mass spectroscopy were used to determine the selectivity of this reaction. Studies with Auger revealed that the ratio of chlorine atoms to iodine atoms on the Al(111) is 0.32 +/- 0.1 at low (0.42 +/- 0.002) surface coverage. TOF studies also show that chlorine atoms are the only species scattered from the surface after ICl interacts with

Al(111). ICl chemisorbs onto the aluminum surface by two mechanisms, abstractive chemisorption and dissociative chemisorption. In addition, these results indicate that iodine-selective abstraction, in which the iodine atom of ICl chemisorbs to the aluminum surface while the chlorine atom is ejected into the gas-phase, is the dominant mechanism in this reaction. Iodine-end first collisions are more reactive than chlorine-end first collisions because the LUMO of ICl is primarily composed of iodine atomic orbitals, and it is the LUMO that interacts with the harpooning electron from the surface.

The remote dissociation of O₂ and NO on Al(111) is more complicated because two charges must be transferred to break the internal molecular bonds. We have used hypersonic molecular beams to probe the reaction dynamics with scanning tunneling microscopy (STM). STM images of the Al(111) surface dosed with low energy (0.025 eV) O₂, show single isolated O-Al chemisorption sites while STM images of the surface dosed with high energy (0.5 eV) O₂ reveal pairs of oxygen adatoms. The data is consistent with abstractive chemisorption of O₂ (formation of O-Al + an ejected O-atom) at low translational energy and dissociative chemisorption at high translational energy.

In a complimentary study, the reaction dynamics of the NO/Al(111) system were probed. The dissociative sticking probability of an oriented molecular beam of NO was measured as a function of incident molecular orientation and translational energy. The data show that the molecule reacts with a higher probability when the N-end is preferentially directed towards the Al(111) surface. In contrast, at low surface coverage, Auger electron spectroscopy (AES) indicates that O-Al forms preferentially over N-Al. In a simple model, an electron harpoons from the metal to the N-end of the molecule. The NO molecular ion is attracted to the surface by its image charge. Next, the molecule must rotate 180° in order to accept a second charge transfer from the surface. Finally, the intramolecular bond breaks and oxygen is deposited onto the surface while nitrogen is ejected into the gas phase.

5. PERSONNEL SUPPORTED:

a. Graduate students

Andrew Komrowski (B.S. Dartmouth University)
Kharissia Pettus (B. S. Univ. of Virginia)

b. Postdoctoral Associates

Yong Liu (Ph.D., Southampton University with Prof. Neville Jonathan)

6. PUBLICATIONS

Chemical Selectivity in the Remote Abstractive Chemisorption of ICl on Al(111) by Kharissia A. Pettus, Peter Taylor, and Andrew C. Kummel (Disc. of the Faraday Society, 117; In Press).
Abstractive Chemisorption of O₂ on Al(111); M. Binetti, O. Weisse, E. Hasselbrink, A. J. Komrowski, A. C. Kummel

7. INTERACTIONS/TRANSITIONS

a. Meetings:

Andrew Kummel attended the U. of Florida MURI review in January 1999.
Andrew Kummel attended the U. of Florida MURI review in Feb. 2000).
Andrew Kummel, Andrew Komrowski attended the Faraday Discussion 117 in August 2000

8, NEW DISCOVERIES

none

9. HONORS/AWARDS

Kummel's STM work was highlighted in both Physical Review Focus and in a perspective in Science Magazine.

Final Technical Report

Equipment Acquired under F49620-99-1-0115

"DURIP 99 Instrumentation for Deposition and Etching of Ferromagnetic Nanoparticles"

Principal Investigator: Andrew C. Kummel

Grantee: The Regents of the University of California, University of California, San Diego

<u>Name of Equipment</u>	<u>Manufacturer</u>	<u>Cost</u>
Upgrade LabVIEW	National Instruments	\$3,043.34
Mechanical Pump	BOC Edwards	\$2,050.48
RV3 Mechanical Pump	BOC Edwards	\$1,402.82
3 Pentium II processors	CompUSA	\$5,701.13
Mass Spectroscopy System	Hiden Analytical	\$66,550.85
RV3 Mechanical Pump	BOC Edwards	\$1,513.54
VG-EX05 Ion Gun	Nashua Corp	\$16,162.50
Fabrication Quadrupole & Ion Gun Installation		<u>\$1,844.67</u>
Total Equipment Costs		\$98,269.33