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Two Stage Growth of Dispersed Nanoparticle Layers Suitable for Giant Magnetoresistance Sensors

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13. ABSTRACT (Maximum 200 words)
During this award, accomplishments were made in two areas: deposition of anisotropic ferromagnetic nanoparticles and etching of metallic materials. (a) The grantee developed a technique to deposit partially anisotropic Fe nanoparticles, 200 x 70 x 80 nm 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 etching Fe particles deposited on Ag substrates. (b) The grantees also investigated the basic mechanisms of etching of Ag(111) by a halogen gas, ICl. Halogen etching of metallic materials is a critical step in fabrication of magnetic sensors, spin valves, and giant magnetoresistive sensors. They found that for ICI/Ag(111) the primary chemisorption process is remote dissociation in which the substrate harpoons in incoming ICI molecule with an electron. The dominant chemisorption process is abstraction in which ICI deposits the iodine atom onto the surface while the chlorine is ejected back into the gas phase.

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1. COVER SHEET: FINAL REPORT ON AFOSR GRANT

PIs: ANDREW KUMMEL and FRED SPADA:

Title: "Two Stage Growth of Dispersed Nanoparticle Layers Suitable for Giant Magnetoresistance Sensors"

Grant#: F49620-98-1-0312

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1.5 ABSTRACT:

During this award, accomplishments were made in two areas: deposition of anisotropic ferromagnetic nanoparticles and etching of metallic materials. (a) The grantees developed a technique to deposit partially anisotropic Fe nanoparticles, 200 Å x 70 Å x 8Å 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 primarily 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.

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 use in giant magnetoresistance devices in order to work collaboratively with the nanomaterials MURI at the Univ. of Florida.

3. STATUS OF EFFORT:

Several critical milestone 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 have been prepared and examined with STM and Auger electron spectroscopy. (3) Fe nanoparticles has been deposited on the Ag(111) substrates and examined with STM and Auger electron spectroscopy. (4) Arrays of spatially anisotropic Fe nanoparticles, 200 Å x 70 Å x 8Å 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) We have completed a detailed study of halogen chemisorption and etching on aluminum, a low work function metal. A comparison will be made to iron in the next year.

4. ACCOMPLISHMENT/NEW FINDINGS:

Upon receipt of our AFOSR grant in March 1998, we ordered a 4 rod electron beam deposition source. This source will enable us to deposit up to four materials simultaneously. 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-annalening 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.

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; Accepted).

7. INTERACTIONS/TRANSITIONS

a. Meetings:


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.