1. DOE award # and name of the recipient (institution)

Award #DE-FG02-08ER46507, West Virginia University Research Corporation

2. Project Title and name of the PI

Hydrogen Absorption in Pd-based Nanostructures

David Lederman, Department of Physics, West Virginia University

3. Date of the report and period covered by the report

Date of report: October 22, 2012

Period Covered by the Report: July 1, 2008 – June 30, 2012

4. Participating National Laboratory

Los Alamos National Laboratory

5. Project abstract

Pd is known to absorb hydrogen. Molecules are normally chemisorbed at the surface in a process where the molecule breaks into two hydrogen atoms, and the protons are then absorbed into the bulk. This process consists of electron filling holes in the Pd 4d band near the Fermi energy, which due to the high density of states at the Fermi energy, is an energetically favorable process.

Our aim with this project was to determine possible changes in magnetic properties with Pd nm-length-scale thick layers intercalated by magnetic materials. Before the start of this work, the literature indicated that there were several possible scenarios by which this could happen: i) the Pd will be magnetized due to a proximity effect with nearby magnetic layers, resulting in changes in the magnetization due to H₂ absorption; ii) some H will be absorbed into the magnetic layers, causing a change in the magnetic exchange interactions; or iii) absorption of H₂ will cause an expansion of the lattice, resulting in a magnetoelastic effect which changes the magnetic properties.

Figure 1 Model of superlattice structure, where N is the number of repeat units.

6. Research accomplishments

• Sample growth and preliminary characterization

We have grown several series of Co/Pd superlattices on Al₂O₃ via sputtering after optimizing the growth conditions. The structure of one typical superlattice is illustrated in Fig. 1. The high angle x-ray diffraction patterns (Fig. 2) indicated a very high level of crystallinity and the AFM images (Fig. 3) showed very smooth surfaces.

- **Magnetic Measurements**

The magnetization measurements were performed in a Vibrating Sample Magnetometer (VSM) in helium and hydrogen atmosphere in order to investigate the changes in magnetic properties. The measurements demonstrated that the magnetic properties of the samples depended significantly on the thickness of the Co/Pd layers in the superlattice. The samples exhibited a wide variety of changes in the coercivity, remanent and saturation magnetization upon hydrogen absorption, which were dependent on the layers' thicknesses, as shown in Fig. 4.

- **Magneto-transport measurements**

Electrical transport properties were measured using a four-point contact technique in current-in-plane configuration on the multilayer samples. The measurements were carried out with in-plane and out-of-plane geometries. The samples exhibited changes in the electrical resistance upon hydrogen absorption which were dependent on the layers' thicknesses. Fig.5 shows a typical graph for an out-of-plane geometry.

- **Neutron scattering experiments**

In-situ unpolarized and polarized neutron reflectometry (PNR) measurements were performed in air and in deuterium at room temperature and one atmosphere pressure on the ASTERIX spectrometer at the Manuel Lujan Neutron Scattering Facility at Los Alamos National Laboratory. The experiments were performed under the supervision of Dr Michael Fitzsimmons from 5th to 13th July 2009 and October 19th to October 27th 2009, with the assistance of graduate student Kineshma Mubodh of WVU. The preliminary results obtained from the first experiment helped us redesign our experiments and enabled us to produce conclusive results on our second attempt.

The structure of the sample measured in October 2009 was [Pd (22 Å)/ (Pd(16.4 Å)/Co(7.16 Å))₄₀/Pd(27 Å)]. The unpolarized neutron data were fitted to extract the structural changes that occur upon deuterium absorption. The data were fitted at West Virginia University

by K. Munbodh under the supervision of Prof. David Lederman. Fig. 6 (a) and (b) shows the measurements in air and in deuterium respectively and the associated fits. The fitting parameters and the associated error bars are shown in Table I. The scattering length density (SLD) profile (Fig. 7) generated from the fits allowed us to make conclusions about the modulation of chemical composition within the sample. It can be seen that upon deuterium absorption, we found a definite increase in the scattering length of the palladium in the stack.

Figure 2 Typical high angle x-ray diffraction pattern with highly oriented growth in the [111] direction.

Figure 3 AFM image of the multilayer of total thickness 97.1 nm and rms roughness of 0.49 nm.

magnetization. The results obtained from the fits and the associated error bars are illustrated in Table II. The results show that there is an overall increase in the magnetization of the sample, which agrees within experimental error with the VSM measurements.

• Conclusions

The results showed that there is a change in the magnetic properties of the Co/Pd supper lattice upon deuterium absorption. The change in magnetic properties can be attributed to electron transfer to the band structure of the cobal-rich layers that is induced by the absorption of deuterium in the palladium layers. The results show that this device can be used as a hydrogen sensor.

The polarized measurement was performed using neutrons with polarization states parallel (up) and antiparallel (down) to the 6.5 kOe magnetic field parallel to the sample surface. With 40.7 % of the magnetization vector perpendicular to q , the PNR was used to determine the magnetic profile before and after the deuterium absorption. The spin-up data showed no Bragg peak whereas the spin-down data showed the presence of a Bragg peak and a half-order Bragg peak which suggests that some of the magnetic scattering has a period that is twice the nuclear period as shown in Fig 8 and 9. The model used for fitting the magnetic data is illustrated in Fig. 10 where the two adjacent Co and Pd layers are assumed to have different

Table I: Fitting parameters obtained from the unpolarized data in air and in deuterium.

Parameters	In air (Å)	In deuterium (Å)
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Pd buffer thickness	22.85 ± 1.80	36.93 ± 1.42
Co thickness	7.16 ± 0.48	7.99 ± 1.11
Co roughness	2.35 ± 1.65	5.54 ± 2.09
Pd thickness	16.38 ± 0.51	15.52 ± 1.12
Pd roughness	1.67 ± 0.73	3.73 ± 0.96
Pd top thickness	27.6 ± 4.70	36.05 ± 2.34
Pd top roughness	7.47 ± 1.10	3.19 ± 1.73
Scattering length Pd top	$(6.2 \pm 0.14) \times 10^{-5}$	$(6.2 \pm 0.12) \times 10^{-5}$
Scattering length Pd stack	$(5.43 \pm 0.03) \times 10^{-5}$	$(5.65 \pm 0.07) \times 10^{-5}$
Scattering length Pd bottom	$(6.34 \pm 0.17) \times 10^{-5}$	$(6.38 \pm 0.10) \times 10^{-5}$

Table II: Layer resolved magnetic structure in air and deuterium.

Layer	M (Air) (μ_B)	M (Deuterium) (μ_B)
Co 2	0.29$\pm$ 0.01	0.31$\pm$ 0.01
Pd 2	0.17$\pm$ 0.01	0.17$\pm$ 0.01
Co 1	0.34$\pm$ 0.02	0.40$\pm$ 0.01
Pd 1	0.26$\pm$ 0.01	0.29$\pm$ 0.02

7. A list of papers (already published, in press, submitted) in which DOE support is acknowledged.

1. K. Munbodh, F. A. Perez, C. Keenan, D. Lederman, M. Zhernenkov, and M. R. Fitzsimmons, Effects of hydrogen/deuterium absorption on the magnetic properties of Co/Pd multilayers, *Phys. Rev. B* **83**, 094432 (2011).
2. K. Munbodh, M. Cheon, D. Lederman, M. R. Fitzsimmons, and N. R. Dilley, “Interface coupling between ferromagnets and random and dilute antiferromagnets, *Phys. Rev. B* **84**, 214434 (2011).
3. K. Munbodh, F. A. Perez, and D. Lederman, “Changes in the magnetic properties of Co/Pd multilayers induced by hydrogen absorption”, *J. Appl. Phys.* **111**, 123919 (2012).
4. D. Diaz-Droguett, K. Munbodh, F. A. Perez, S. Ducatman, and D. Lederman, “Magnetotransport properties of Co/Pd multilayers as a function of hydrogen absorption”, in preparation.

8. People working on the project

Kineshma Munbodh: Graduate student working full time on the project, July 1, 2008 – May 15, 2012.

Felio Pérez: Postdoc working full time on the project (January 1, 2009 – December 31, 2011).

Sam Ducatman: Undergraduate student, summer 2009.

Donovan Diaz-Droguett: Postdoc working on transport measurements April 2012-August 2012. Not funded by DOE but contributed to the project.

9. Updated list of other support

Note: none of the projects below are related to the DOE project which is the subject of this report.

Project/Proposal Title: **MRI: Acquisition of a Pulsed Laser Deposition System for Applications in Physics, Chemistry, Biology, Health Sciences, and Engineering** (Lederman PI, Urazhdin, Wu, Holland, Holcomb Co-PIs)

Source of Support: **NSF-MRI**

Total Award Amount: **\$468,389** Total Award Period Covered: **10/01/2010 – 09/30/2012**

Location of Project: **West Virginia University** Person-months/year: 0.5

Project/Proposal Title: **Bionanotechnology for Public Security and Environmental Safety, NSF EPSCoR RII** (P. Hill, PI, C. Peterson, Co-PI, D. Lederman, Technical PI, many other participants)

Source of Support: **NSF EPSCoR/WVEPSCoR**

Support: **Current**

Total Award Amount: **\$20,000,000** Total Award Period Covered: **08/15/2010 - 08/14/2015**

Location of Project: **West Virginia University, Marshall University, West Virginia State University**

Person-months/year: 1.0

Project/Proposal Title: **REU Site: Multifunctional Nanomaterials** (Richards-Babb, PI; Lederman Co-PI)

Source of Support: **NSF-REU**

Total Award Amount: **\$315,000** Total Award Period Covered: **04/15/2010 – 03/31/2013**

Location of Project: **West Virginia University** Person-months/year: 0.5

Project/Proposal Title: **Protein-Protein Interactions Determined by Selective Protein Manipulation** (Gannett Co-I, Lederman, Wu Senior Participants)

Source of Support: **NIH-R01**

Total Award Amount: **\$393,000** Total Award Period Covered: **09/30/2009 – 09/29/2012**

Location of Project: **West Virginia University** Person-months/year: 0.5

Project/Proposal Title: **Magnetic and Magnetoelectric Interactions and Excitations in Ideal Antiferromagnetic Systems** (Lederman PI)

Source of Support: **NSF-DMR**

Total Award Amount: **\$230,000** Total Award Period Covered: **09/01/2009 – 08/31/2012**

Location of Project: **West Virginia University** Person-months/year: 0.5

10. Cost status

Approved budget: \$449,944 July 1, 2008 – June 30, 2011, with a no-cost extension to June 30, 2012.

Costs incurred by 06/30/2012: \$449,944 (including encumbrances).

Cost share: \$24,000 for equipment – full amount spent.