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FY04 LDRD Final Report: Properties of Actinide Nanostructures

A. V. Hamza, T. W. Trelenberg, J. G. Tobin

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Properties of Actinide Nanostructures
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Alex Hamza, Principal Investigator

Abstract

Two papers completely describe the objectives and work performed in this laboratory directed research and development (LDRD) project. The first paper published in *Review of Scientific Instruments* (UCRL-JC-152913) describes the purpose, construction, and operation of a novel instrument to produce and characterize actinide nanostructures by pulsed laser deposition. The second paper submitted to *Physical Review B* (UCRL-JRNL-209427) describes our work quantifying the oxidation of pulsed laser deposited depleted uranium nanostructures by following the evolution of the electronic structure.

Introduction/Background

The actinides elements contain electrons in their 5f shell with bonding character ranging from itinerant in the early actinides to localized in the later actinides. Of particular interest is Pu, which lies on the transition point of the bonding/non-bonding character and which can be stepped through this transition with temperature, pressure, or alloying.

Studies of the electronic structure of actinides should ideally be carried out on clean, single-crystalline samples, however, producing single-crystalline samples of sufficient size has proven difficult. Since band mapping, which can discriminate between localized and itinerant behavior, requires knowledge of crystalline orientation, one must study single crystals in which it is possible to determine orientation in addition to the sample being large enough to allow the measurement to be restricted to the area of known orientation. While efforts to grow larger, single-crystal actinide samples have met with some success, isolation of these crystals for study via traditional techniques still presents a problem. In addition, the actinides are highly reactive and oxidize readily even under the best of vacuum conditions.

Another approach is to study thin films grown on a suitable substrate. Crystalline films may be produced, however, the structure observed may be influenced by the substrate and care must be taken to ensure that no significant changes are introduced into the measurement. Our approach was to isolate and analyze readily produced nanocrystallites using microprobe techniques; to identify a crystallite and determine its orientation using an STM (scanning tunneling microscope) and then probe its electronic structure using STS (scanning tunneling spectroscopy). It was further hoped that by mapping out the electronic structure from nanocrystals of various sizes one could separate out the contribution of various correlation effects, as their interaction varies as a function of particle size once the nanoparticles are sufficiently small that quantum effects become noticeable. Pulsed laser ablation was chosen as the method for producing our samples as the production of both high-purity nanoscale material and actinide films (through careful annealing) had been demonstrated. Laser ablated nanocrystallites naturally occur with a range of sizes, so further processing, other than choosing a particle size via an STM scan, would not be required.

One of the chief challenges of this program was to deposit actinide material containing no oxidation or other contamination. Given the high reactivity of the actinide elements, the preparations of clean actinide surfaces can be a difficult task. Such surfaces have been prepared via sputter-cleaning of the surface, laser ablative cleaning of the surface, and plasma deposition. Over the last decade, the availability of compact, low-cost, high-power pulsed laser systems has allowed laser deposition to emerge as a competing technology, which has the added advantage of transferring the stoichiometry of complex target materials to sample substrates in a large number of materials, provided certain conditions are met.

Research Activities

A novel instrument for the synthesis and analysis of nanoparticles and ultrathin films of Pu and other actinides has been constructed. Owing to the highly toxic and radioactive nature of samples such as Pu, significant safety measures must be taken in the deposition of the actinide samples via laser ablation. Analytical capabilities include *in-situ* photoelectron spectroscopy, low energy electron diffraction (LEED), scanning tunneling microscopy (STM), and scanning tunneling spectroscopy (STS). See reference 1 for more detail.

Depleted uranium samples were ablated using five nanosecond pulses from a Nd:YAG laser. Films of ~1600Å thicknesses were produced and found to deposit with an angular distribution typical of a completely thermal ablation (\cos^2). The films remained contiguous for many months in vacuum but blistered due to tensile stress induced in the films several days after being brought into air. While under vacuum (2×10^{-10} Torr base pressure) the films were allowed to oxidize from the residual gases, of which water vapor was found to be the primary oxidizer. During the oxidation the samples were observed with both X-ray and Ultraviolet Photoemission Spectroscopy (XPS and UPS) and were found to oxidize following Langmuir kinetics. That a 2D surface growth model described the oxidation indicates that even at these low pressures oxygen accumulation on the surface is a much faster process than diffusion into the bulk. While bulk diffusion did occur, the oxygen present at the surface saturated the measurements taken using photoemission and diffusion was difficult to observe. See Reference 2 for more detail.

Exit Plan

We recruited two excellent post-doctoral researchers to this project. One of them was subsequently hired by CMS and is matrixed to DNT projects on actinide science and ageing. The pulsed laser deposition apparatus has also been transferred to the enhanced surveillance program for further investigations of actinide nanostructures.

References

- [1] T. W. Trelenberg, S. C. Glade, T. E. Felter, J. G. Tobin, A. V. Hamza, "Instrument for the investigation of the nanostructure of Pu and other actinides," *Review of Scientific Instruments* 75 (3): 713-718 MAR 2004.
- [2] T. W. Trelenberg, S. C. Glade, J. G. Tobin, and A. V. Hamza, "The production and oxidation of uranium nanoparticles produced via pulsed laser ablation," *Physical Review B*, submitted.