

## **Determining the Feasibility of Single Crystal Actinide Oxide Thin Films for Solid State Fast Neutron Detection – April 2011 – Investigator X**

**Project Description:** The primary goal of this project is to determine whether there exists a fundamental physical and/or electronic structure barrier in the use of actinide oxide thin films for direct conversion solid state neutron detectors. Development of actinide oxides in this application context is worth investigation because of the promise of solid state ultra-low noise fast neutron detection (no gas or moderator).

**Objective:** The scope of this project is to determine whether there is a fundamental limit on carrier mobility and stoichiometry stability in actinide oxide films, in the context of application, focusing primarily on urania (UO<sub>2</sub>). As demonstrated in the peer reviewed literature, the semiconductor properties of UO<sub>2</sub> vary with thin film preparation and state of crystallinity; we therefore propose to minimize electrical carrier scattering paths and free energy differences (to find the upper limit on the properties of interest) by epitaxially growing single crystal films of UO<sub>2</sub> by reactive electron beam evaporation. The electrical carrier transport performance of these films, with a focus on ion and electron mobility and interfacial work function, will be determined as described below.

**Application:** The appeal of using uranium, plutonium or neptunium dioxide films as the active material for direct conversion solid state fast neutron detection is the very high-energy yield (>165 MeV) transferred from the daughter fragments upon neutron-induced fission as well as neutron multiplication (n,xn) that can lead to effective moderation. The daughter fragments' energy can only be released through the absorption of a neutron; when combined with a very high lower level discriminator setting (e.g., 10 MeV), an actinide-based heterostructure device would be made blind to nearly any non-neutron background (e.g., gammas, protons, or internal alphas). Additionally, the use of this detector for fission spectrum neutrons (given the relatively high cross section for fast neutrons and high density of the actinide oxides) means that large volumes of moderator (e.g., polyethylene) are not required, changing the game from thermal solid state detectors considerably. To the investigators knowledge, there is no other solid state neutron detector technology for fast neutrons. Further, the conversion and subsequent separation of electron-hole-pairs generated from these highly energetic daughter fragments is two to three orders of magnitude greater than the energy available from the moderate energy ion products following neutron scattering or capture by <sup>1</sup>H, <sup>3</sup>He, <sup>6</sup>Li, <sup>10</sup>B, <sup>113</sup>Cd, or <sup>157</sup>Gd. This translates to higher noise level allowability and less expensive electronics because the pulse height is so large.

**Prior Work:** The semiconductor properties of polycrystalline UO<sub>2.00</sub> and doped UO<sub>2</sub> and transport mechanisms in hypostoichiometric (congruent), stoichiometric and hyperstoichiometric UO<sub>2</sub> have been established [1-15]. Electronic structure calculations of the Mott insulators NpO<sub>2</sub> and PuO<sub>2</sub> have been published [15-20] but very sparse experimental work concerns the semiconductor properties in these latter actinides. Additionally, there currently is no data concerning isotopic variation, e.g. U-238 versus U-235, Np-237 versus Np-238 for applications in neutron detection.

It should be stated that uranium oxides are proposed to yield intrinsic electronic properties equivalent to or much better than the intrinsic properties of conventional Si, Ge, and GaAs semiconductor materials [1] and that both diodes and transistors have been demonstrated using thin films of  $\text{UO}_2$  [1]. However, there appears to be significant differences in the electrical carrier transport properties depending on the preparation and/or final local physical structure of the thin film. These thoughts are corroborated by an early paper [6] which compared the photoconductivity of an adherent powder thin film to a polycrystalline film (where the grain boundary and trapping center density is significantly differentiating) finding that the powder film would not yield a photocurrent upon UV/Vis incident light. Such a revelation is not intuitive, and it is not clear from the open literature that anyone has tried to remove these grain boundary and trapping center effects. Thus we suggest that the most direct means of determining whether carrier mobility is a showstopper is to initiate and focus our study of actinide oxide films with single-crystal, thin-films. There is currently only one satisfactory method of producing such films using solution methods [23], however, these films are very small, it is still difficult to control film thickness using the method, and the preparation will change depending on the actinide. We propose reactive electron beam evaporation as it is currently the industry standard for epitaxial growth and the best available method to grow single crystals and control film thickness (which will also be amenable to large area deposition if desired down the road).

**Challenges to actinide oxide development as semiconductor materials:**

Depending on the dopant and its concentration our starting actinide  $^{238}\text{UO}_{2.00}$  can become hypostoichiometric (congruent), which changes the electronic structure in ways that may or may not prove useful.

The electrical conductivity of  $\text{UO}_{2.001}$  vs that of  $\text{UO}_{1.994}$  varies by four orders of magnitude (24). The lack of accurate determination of stoichiometry likely explains the large variability in electrical resistivity reported in the literature for urania. It is certainly not currently appreciated what the optimal oxide stoichiometry is and range (gap, resistivity, mobility, stability) for a given application. Consequently, electrical properties of uranium oxide semiconductors should be measured with attention paid to such parameters as oxygen content. Oxidative changes may be less of a concern for  $^{238,239}\text{Pu}$  or  $^{237,238}\text{NpO}_2$  because of their lower susceptibility to oxidation even at high temperature.

The mechanism responsible for electrical carrier mobility is currently not understood but has been for Eu and Ce doped hyperstoichiometric  $\text{UO}_2$  confirmed as small polaron hopping [25], nor is the relationship to hypostoichiometry where the resistivity tends to be lower. It is also not understood how an isotope with higher specific activity (than U-238) will impact material resistivity and electron mobility. To exacerbate the problem, accurate band structure calculations that might lend some insight to structure functional relationships of actinide oxides are presently not developed enough due to the strong electron correlation of the actinide 5f orbitals

**Proposed Research:** As described above, we propose to overcome several of the issues associated with material preparation, e.g. pellet, powder, polycrystalline, single crystal by growing crystals of  $\text{UO}_2$  using reactive electron beam evaporation to grow single crystals, control oxidation, and control film thickness. The stoichiometry as a function of thermal treatment conditions by environmentally controlled XRD. We intend to determine valency, work function, and valence band offset as a function of stoichiometry by XPS and UPS and measure the approximate band gap as a function of stoichiometry by UV/Vis. Resistivity and mobility measurements will be made at room temperature and as a function of temperature at selected stoichiometries by the four point Hall technique. Such measurements made under rigorously inert atmosphere or vacuum will extract a rigorous electrical carrier transport picture for  $\text{UO}_2$  and higher actinide oxide films.

**Deliverable:** The investigators will deliver reports and peer reviewed publications of the electronic structure, and electrical carrier transport structure as a function of the growth conditions of the actinide oxide pellets thin films. The isotopes included will depend on programmatic interest.

## References

- [1] T. T. Meek, B. Roedern, "Semiconductor devices fabricated from actinide oxides," *Vacuum* **83** (2009) 226–228.
- [2] T.T. Meek, B.G. von Roedern and M.J. Haire, "Some electrical properties of  $\text{UO}_2$  - Part I", Transactions of the American Nuclear Society 88 (2003) 416-418.
- [3] P.W. Winter, "The Electronic Transport Properties of  $\text{UO}_2$ ", J. Nucl. Mats. 161 (1989) 38-43.
- [4] J.M. Casado, J.H. Harding and G.J. Hyland, "Small-Polaron Hopping in Mott-Insulating  $\text{UO}_2$ ", J. Phys.: Cond. Matt. 6 (1994) 4685-4698.
- [5] P. Ruello, K.D. Becker, K. Ullrich, L. Desgranges, C. Petot and G. Petot-Ervas, "Thermal Variation of the Optical Absorption of  $\text{UO}_2$ : Determination of the Small Polaron Self-Energy", J. Nucl. Mats. 328 (2004) 46-54.
- [6] S. Iida, "Photocurrent and Thermal Release Time Studies of Uranium Dioxide", Jap. J. Appl. Phys. 5 (1966) 752
- [7] Richard A. Young, "Model for the Electronic Contribution to the Thermal and Transport Properties of  $\text{ThO}_2$ ,  $\text{UO}_2$ , and  $\text{PuO}_2$  in the Solid and Liquid Phases", J. Nucl. Mats. 87 (1979) 283-296
- [8] J. Schoenes, "Electronic Transitions, Crystal Field Effects and Phonons in  $\text{UO}_2$ ", Physics Reports 63 (1980) 301
- [9] J.C. Killeen, "The Measurement of the Electron-to-Hole Mobility Ratio in  $\text{UO}_2$  and its effect on the thermal conductivity", J. Nucl. Mats. 92 (1980) 136-140.
- [10] Andre Sorriaux, "Evaluation of Forbidden Band and the Acceptor Energy Levels in Natural Uranium Dioxide", Comptes Rendus des Seances de l'Academi des Sciences, Serie B: Sciences Physiques 270 (1970) 77-79.
- [11] Andre Sorriaux and Henri Djerassi, "Electrical Conductivity and Thermoelectric Power of Uranium Dioxide  $\text{UO}_{2+x}$  at High Temperatures", Comptes Rendus des Sciences, Serie B: Sciences Physiques 272 (1971) 1373-1376.
- [12] J. Devreese, R. De Coninck and H. Pollak, "On the Conduction Mechanism in Uranium Dioxide", Physica Status Solidi B 17 (1966) 825-829.
- [13] J.L. Bates, C.A. Hinman and T. Kawada, "Electrical conductivity of uranium dioxide", Journal of the American Ceramic Society 50 (2006) 652-656.
- [14] P. Nagels, M. Denayer and J. Devreese, "Electrical Properties of Single Crystals of Uranium Dioxide", Solid State Communications 1 (1963) 35-40.
- [15] Younsuk Yun, Kwangheon Park, Hunhwa Lim, Kun Woo Song, "Electronic States of Uranium Dioxide", J. Korean Nuc. Soc. 34 (2002) 202-210.
- [16] P. Santini, S. Carretta, G. Amoretti, "Multipolar Interactions in *f*-Electron Systems: The Paradigm of Actinide Dioxides", Reviews Modern. Physics, 81 (2009) 807.
- [17] T. Nishi, A. Itoh, M. Takano, M. Numata, M. Akabori, Y. Arai a, K. Minato, "Thermal conductivity of neptunium dioxide", Journal of Nuclear Materials 376 (2008) 78.
- [18] X. Wu, A.K. Ray "A density functional study of plutonium dioxide", Eur. Phys. J. B **19** (2001) 345.
- [19] A. Seibert, T. Gouder, F. Huber, "Reaction of neptunium with molecular and atomic oxygen: Formation and stability of surface oxides" Journal of Nuclear Materials 389 (2009) 470.
- [20] C. McNeilly, "The Electrical Properties of Plutonium Oxides", J. Nucl. Mat. **11**, 53 (1964).
- [22] A. K. Burrell, T. M. McCleskey, P. Shukla, H. Wang, T. Durakiewicz, D. P. Moore, C. G. Olson, J. J. Joyce, Q. Jia, "Controlling Oxidation States in Uranium Oxides through Epitaxial Stabilization" *Advanced Materials* **19** (2007) 3559–3563
- [23] Thomas M. McCleskey, Anthony K. Burrell, Jia Quanxi and Yuan Lin, "Precursors for the Polymer-Assisted Deposition of Films", (2009) World Patent App. No. WO2009134698.
- [24] Gmelin Handbook, 1979. "Uranium Supplement," Vol. C5.
- [25] S. H. Kang, J. D. Yi, H. I. Yoo, S. H. Kim, Y. W. Lee, Journal of Physics and Chemistry of Solids 63 (2002) 773.