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SEMICONDUCTIVE PROPERTIES OF URANIUM OXIDES

Thomas Meek
University of Tennessee

Michael Hu and M. Jonathan Haire
Oak Ridge National Laboratory

ABSTRACT

Semiconductors that are based on uranium dioxide (or other actinide compounds) appear possible and could offer significant improvements in performance as compared to conventional Si, Ge, and GaAs materials. The energy band gap (forbidden band gap) for uranium dioxide (UO_2) lies between Si and GaAs at the optimum of the band gap vs efficiency curve (1), indicating that one should be able to use uranium oxides to make very efficient solar cells, semiconductors, or other electronic device. The electrical conductivity of intrinsic UO_2 is approximately the same as GaAs (1). The dielectric constant of UO_2 (-22) is nearly double that for Si (11.2) and GaAs (14.1) (2), perhaps making UO_2 better suited for integrated circuits than Si, Ge, and GaAs. The ceramic oxides of uranium (e.g., U_3O_8 or UO_2) can withstand much higher operating temperatures (-2600 K) than can Si or GaAs (<473 K). In addition, oxides are much more resistive to radiation damage, perhaps making uranium oxides more suitable for fabrication of devices used in special (e.g., space and military) applications. Thus, it appears that a new higher performance class of semiconductors are possible: uranium oxide-based semiconductors.

This paper discusses the electronic properties of uranium dioxide and describes the potential performance advantages of uranium dioxide as compared to conventional semiconductor materials. The need for additional fundamental data is discussed. The results of fabricating and testing a uranium-based diode will be presented if the test results are available in time. This work was conducted under the auspices of the U.S. Department of Energy's Depleted Uranium Uses Research and Development Program.

INTRODUCTION

There has never been an electronic device made using an oxide of uranium as a semiconductor. Yet, uranium oxides have intrinsic electrical and electronic properties equivalent to or much better than the intrinsic properties of conventional Si, Ge, and GaAs semiconductor materials. Figure 1 compares the range of UO_2 conductivity to typical ranges of conductivity of common insulators, semiconductors, and conductors (1). Figure 2 gives the electrical conductivity of UO_2 single crystals as a function of temperature. At room temperature, the electrical conductivity of intrinsic UO_2 (3) is approximately the same as a single crystal of silicon and less than the intrinsic electrical conductivity of GaAs. Clearly, UO_2 is an excellent semiconductor material.

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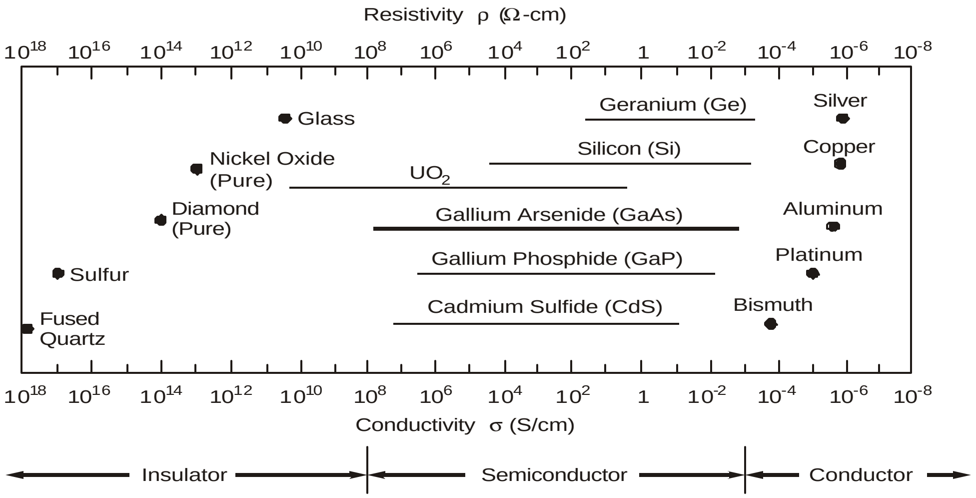

Fig. 1. Comparison of UO_2 Conductivity to Typical Range of Conductivities for Insulators, Semiconductors, and Conductors [Sze 1985].

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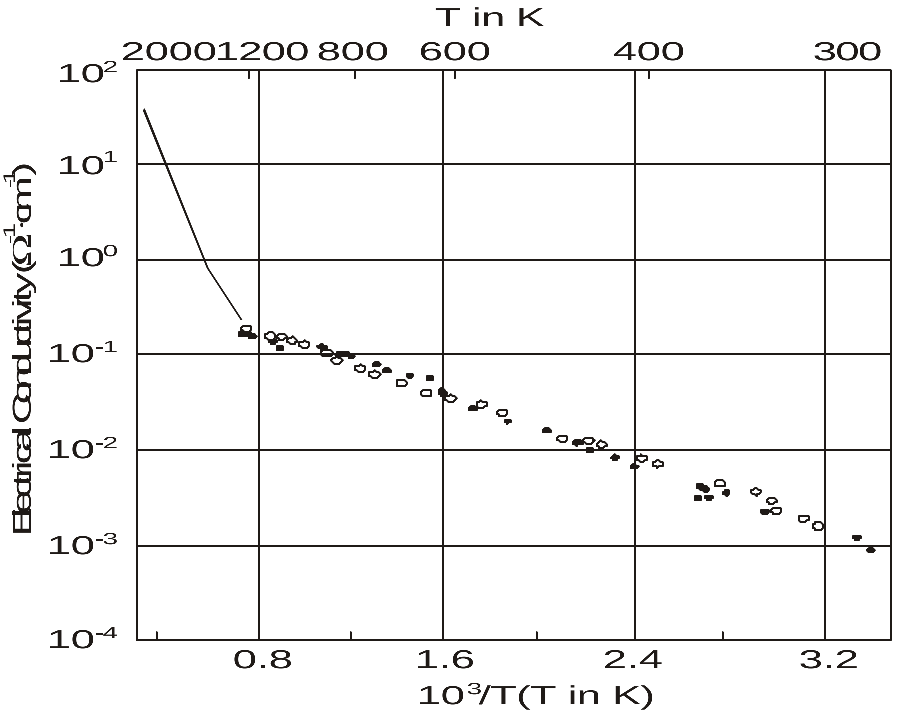

Fig. 2. The Electrical Conductivity of UO_2 Single Crystals as a Function of Temperature [Gmelin 1979].

The solar-cell efficiency vs electronic energy band gap for uranium dioxide is shown in Fig. 3 and is compared to other semiconductor materials (1). The electronic band gap of UO_2 lies near the optimum efficiency, maximum of the curves at - 1.3 eV (2), between Si and GaAs, indicating that UO_2 is a somewhat better semiconductor material than are conventional Si or GaAs materials for solar-cell applications.

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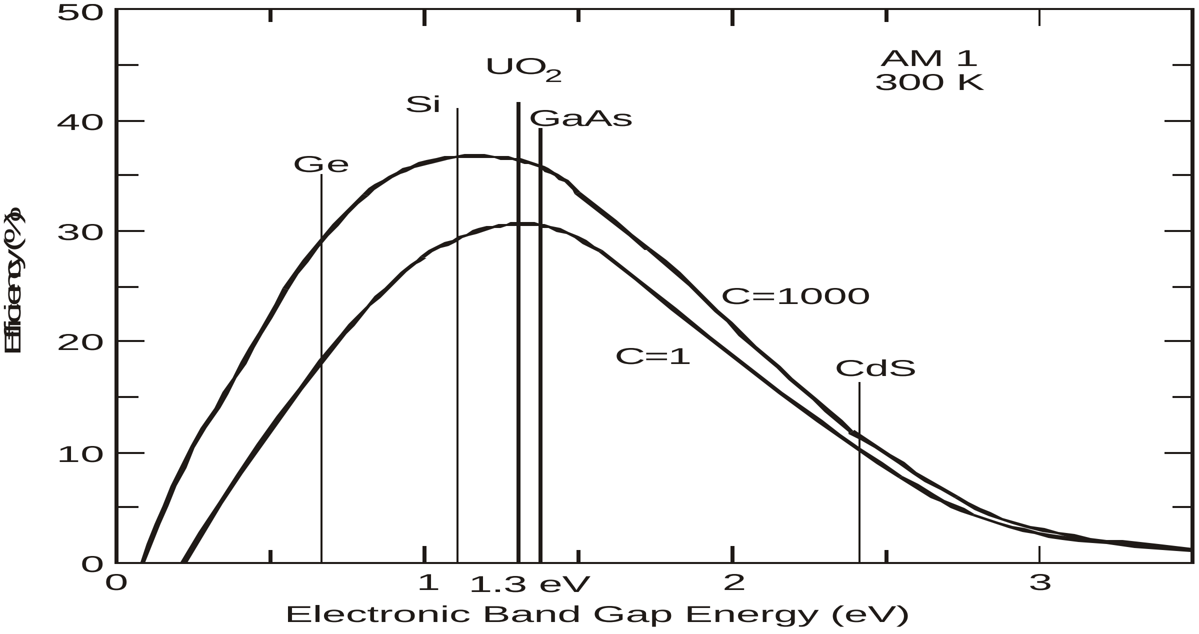

Fig. 3. Ideal Solar-Cell Efficiency at 300K for 1 Sun and for a 1000-Sun Concentration [Sze 1985].

Certain materials in contact with each other produce an electric current when there is a temperature gradient across the junction. The Seebeck coefficient is a measure of this thermoelectric effect. At room temperature (- 300 K), the Seebeck coefficient of uranium dioxide is - 750 µV/K, as shown in Fig. 4. This value is considerably higher than the currently most promising materials Tl_2SnTe_5 and Tl_2GeTe_5 (- 270 µV/K) (4), shown in Fig. 5. Other factors, such as electrical and thermal conductivity, are important along with the Seebeck coefficient, but these factors also have favorable properties, as previously discussed. Thus, uranium oxides might be used as a thermoelectric material and be applied in next generation small-scale refrigerators and power generation applications.

The dielectric constant of UO_2 is nearly double that of Si and GaAs—22 at room temperature as compared to 12 and 14 for Si and GaAs, respectively (2). This characteristic may make uranium oxides suitable for making higher density integrated circuits with higher breakdown voltages than current silicon-based electronics, without suffering complementary metal oxide semiconductor (CMOS) tunneling breakdown due to smaller nanometer size features. Thus, uranium oxide electronics may offer better integrated circuit performance than do conventional Si or GaAs material devices.

A literature search reveals that the work-function parameter has never been measured for UO_2. The value of the work function parameter for various elements are shown in Fig. 6. Also, the solubility of various dopant materials in uranium oxides has not been measured. This information indicates that uranium oxides have never seriously been considered as semiconductor devices. Many electronic parameters need to be measured again with the intent of using uranium oxides as semiconductor material.

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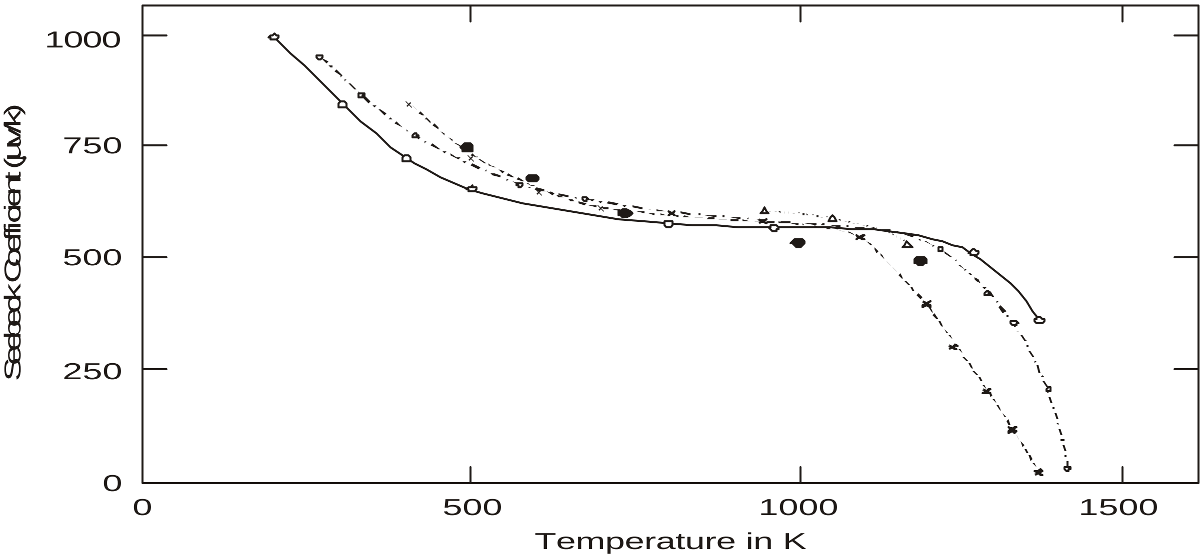

Fig. 4. Thermoelectric Property of Uranium Dioxide [Gmelin 1979].

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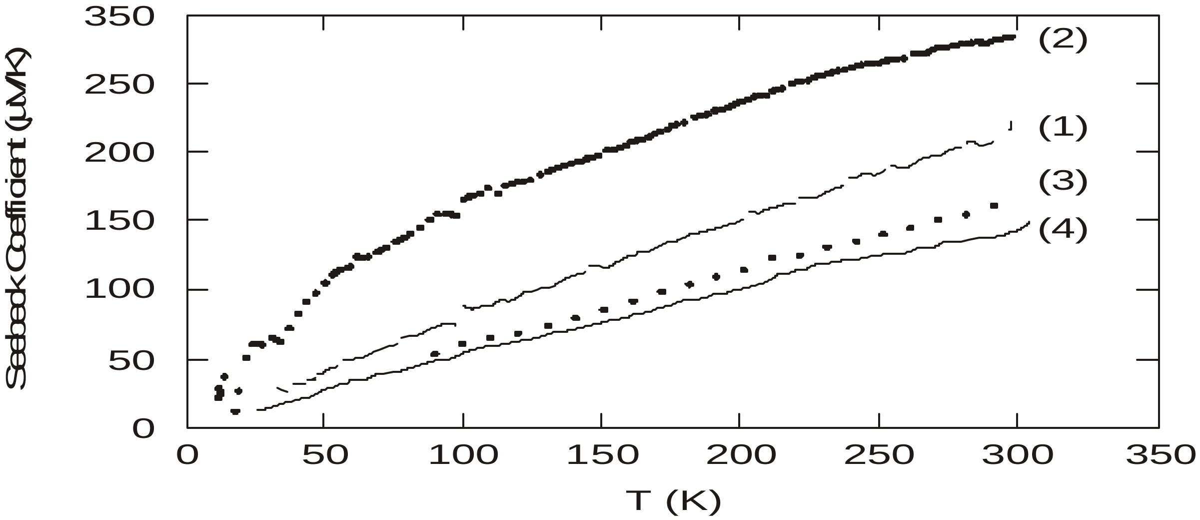

Fig. 5. Data for the Most Promising Thermoelectric Materials: (1) Polycrystalline TST, (2) TGT, (3) Hot Pressed TST, (4) TST Single Crystal [Sharp].

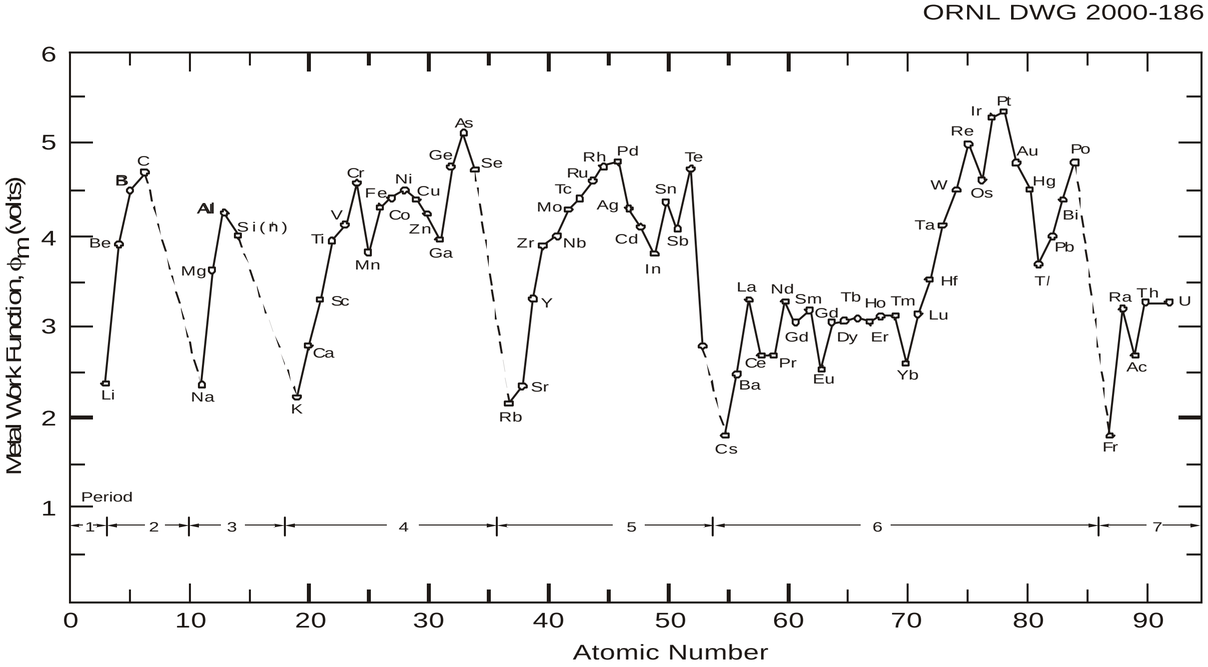

Fig. 6. Metal Work Function for a Clean Metal Surface in a Vacuum Versus Atomic Number [Sze 1985].

URANIUM-BASED ELECTRONIC DEVICES

The implications of these data are discussed for several semiconductor devices.

Solar Cells

The electronic bandgap of UO_2 is - 1.3 eV (at room temperature) (2), which is between Si and GaAs and is very near the peak of the efficiency vs E_g curve, as shown in Fig. 3. Thus, UO_2 should give the highest solar-cell efficiency possible. The electronic band gap for UO_2, U_3O_8, and U_2O_2 are such that each of these materials can be made into a photovoltaic device that can convert optical and infrared (IR) radiation into electrical energy.

A solar cell is a simple, semiconductive, energy conversion device. The performance of such a device is described in terms of conversion efficiency—how well incident solar radiation is converted into usable electrical power. Power is measured by multiplying short circuit current by open-circuit voltage.

While various solar-cell designs are feasible, perhaps the easiest to fabricate is a Schottky-barrier solar cell. This type of solar cell makes use of the different work functions of the oxide material and of the other contact material forming the diode. The device is fabricated by using polycrystalline or single-crystal uranium dioxide. Typically, a thin, metal-film top contact is deposited via a conventional sputtering technique, and an ohmic back contact is made with gallium.

Thermoelectric Devices

When a junction is made between a uranium oxide material and another thermoelectric material (e.g., a metal), a thermoelectric cell is made. If a temperature gradient is established across the junction, an electric current is generated via the Seebeck effect. If optical or IR radiation is incident on the material, additional current is generated across the interface. For example, one material might be exposed to the inside of a refrigerator and the other to ambient room conditions in a next generation refrigerator. Or, one material may be exposed to an inside temperature of a spacecraft and the other to ambient cold-space temperature in a power-generation application.

Integrated Circuits

Conventional integrated circuits suffer CMOS tunneling breakdown due to the smaller 2.5-nanometer device size used today. The density of components in microcircuits has grown exponentially since the early days of the industry—doubling every 18 months. To continue this density scaling, the only option is to go to higher dielectric constant materials. Manufacturers must convert to a high dielectric constant material within five years to avoid slackening of the pace of innovation (5). The dielectric constant for UO_2 is 22 at room temperature as compared to 12 for Si and 14 for GaAs (2). This implies that uranium dioxide integrated circuits can be made much smaller (denser) than conventional integrated circuits.

FUNDAMENTAL DATA NEEDED

Before it can be said that uranium-based semiconductors are better than current ones, the electronic and electrooptical properties of uranium oxide single crystals and polycrystals powders and solid materials must be characterized.

Impact of Radioactive Decay

The impact of radioactive decay of ^{238}U and ^{235}U on electronic performance has not been evaluated. Alpha particle decay would introduce helium impurities and might inhibit current carrier mobility and overall electrical conductivity. The very long half-lives of ^{238}U and ^{235}U and subsequent slow decay rate should have little impact on the performance of solar cells and thermoelectric devices, but they could impact high-performance integrated circuits.

Impact of Stoichiometry

The literature indicates that the performance of UO_2 as a semiconductor material is strongly related to its stoichiometry. For example, as shown in Fig. 7, the electrical conductivity of $UO_{2.001}$ vs that of $UO_{1.994}$ varies by four orders of magnitude (3). Thus, there are many fundamental properties of uranium oxide semiconductors that should be re-measured—with close attention paid to such parameters as oxygen content, with the objective of uranium use in semiconductor devices.

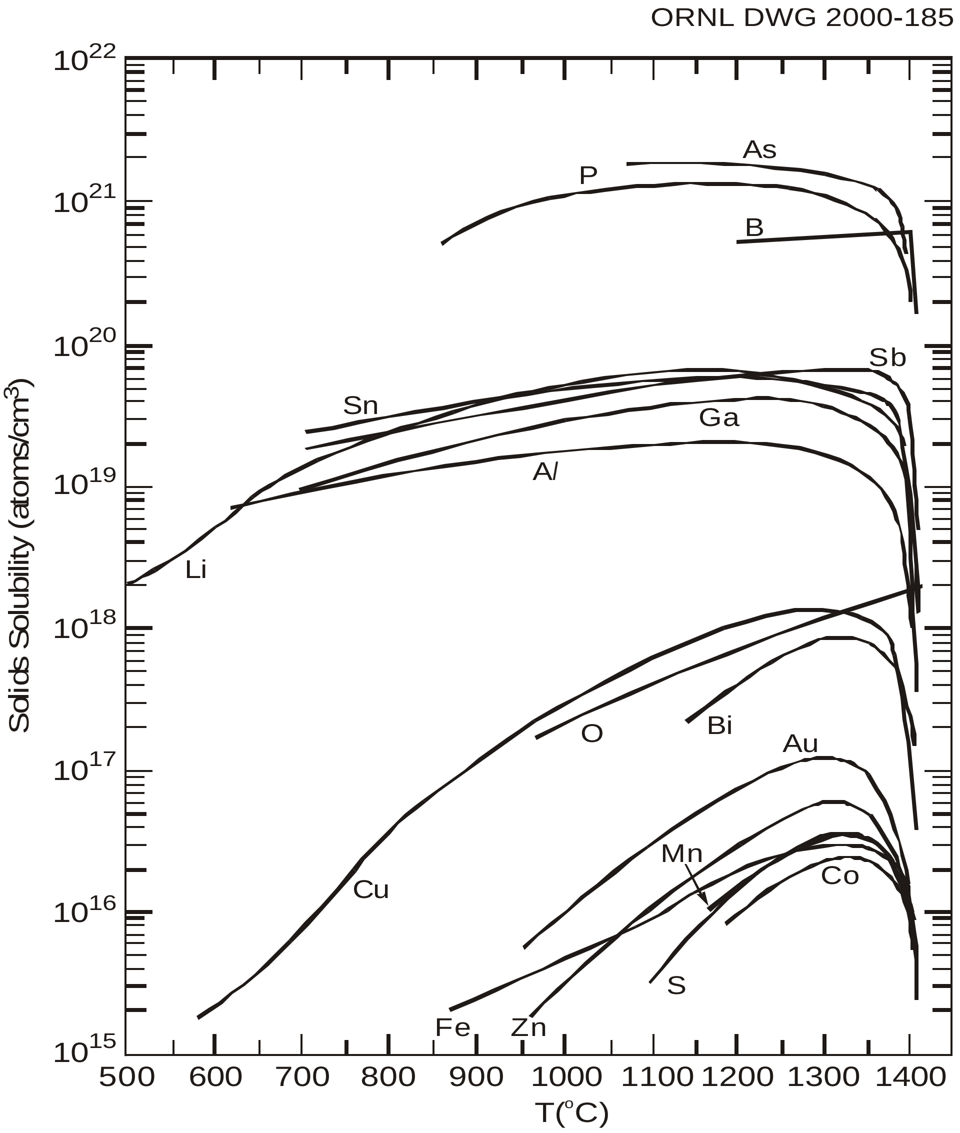

Fig. 7. Solid Solubilities of Impurity Elements in Silicon [Sze 1985].

Dopant Materials

Before uranium-based integrated circuit devices can be designed and fabricated, dopants must be chosen. Figure 8 shows dopant solubility in silicon. Similar curves of impurity solubility in uranium are needed to choose the optimum dopant. But, such curves do not exist.

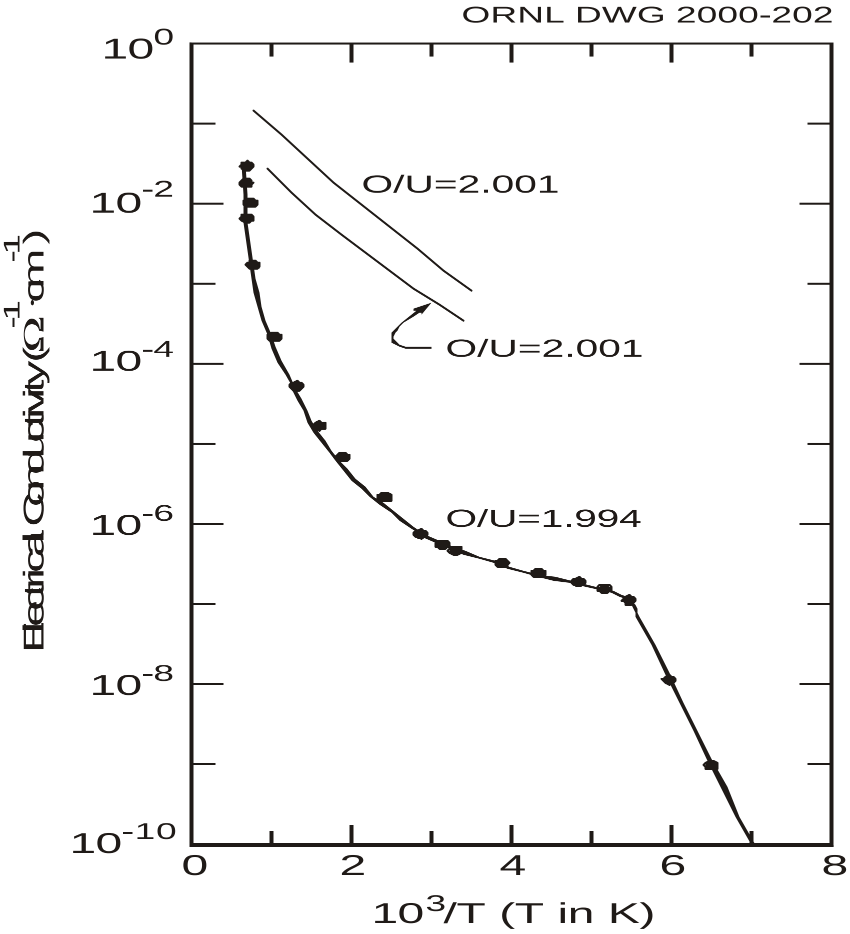

Fig. 8. Electrical Conductivity of UO_2 Single Crystals as a Function of Oxygen Content [Gmelin 1979].

DEPLETED URANIUM CONSUMPTION

Approximately 5,000 t of silicon are processed worldwide each year into electronic devices. If depleted uranium (DU) were used instead of silicon, on an atom-for-atom basis (238/28), this corresponds to 42,000 t/year of DU consumption. There are - 20,000 t of DU produced each year in the United States as tails from uranium enrichment operations. Thus, if all electronic devices were made of uranium, it could consume the yearly production of DU each year.

FABRICATION AND TESTING OF A URANIUM-BASED DIODE

A diode is one of the simplest electronic device. Yet, it is a building block for semiconductor applications. Fabricating and measuring the performance of a uranium dioxide-based diode predict the performance of solar cells, uranium-based transistors, etc. Thus, the evaluation of uranium-based materials in electronics will begin with the simplest electronic device. Proof-of-principle tests will be conducted using a polycrystal UO_2-based diode. The type of dopant material will be based initially on proven dopants used in Si and GaAs. The first dopant material will be niobium. Current vs voltage (I-V) curves will be measured during testing, and the results will be compared to conventional diodes. It is recognized that this initial diode performance may not be optimum because the choice of dopant material is almost arbitrary.

SUMMARY

Uranium oxides have four characteristics that could potentially give them significantly better performance than conventional semiconductor materials: (1) operation at substantially higher temperatures, - 2600 K vs <473 K; (2) a Seebeck coefficient two to three times greater than the most promising current material, implying significantly better performing thermoelectric devices; (3) higher dielectric constant suitable for making integrated circuits; and (4) greater radiation and EMI resistance implying much improved performance for special, e.g. space, applications. However, before it can be said that uranium-based semiconductors are better than current ones, the electronic and electrooptical properties of uranium oxide single crystals and polycrystals powders and solids materials must be characterized. The optimal dopant material must be established by developing metal solubility in uranium curves. Parameters, such as work function, need to be measured.

Proof-of-principle experiments with an uranium diode will be conducted to confirm the theoretical promise of uranium use as a semiconductor material.

ACKNOWLEDGMENT

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