Ion Implantation of UO_2

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January 2002

Submitted to the
Society for the Advancement of Materials and Process Engineering (SAMPE)
2002 Symposium/Exhibition
Long Beach, California
May 12–16, 2002

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*Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725.

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ABSTRACT

Polycrystalline samples of uranium dioxide (UO_2) were implanted with several dopants using ion energies ranging from 140 Kev to 300 Kev. Deposition times ranged from a few seconds to over two hours: Dose levels ranged from 8×10^{11} to 5×10^{16} atom/cm^2 at depths of from 0.05 microns to 0.21 microns. Elements implanted were Sb, Te, B, P, S, and Al. The affect of these dopants on the electrical conductivity of UO_2 is reported. Sample electrical conductivity was measured using the van der Pauw four-point probe technique. Only unannealed samples were analyzed.

KEY WORDS: Ceramic Materials/Composites, Electrical and Electronic, Resistivity

1. INTRODUCTION

Uranium dioxide has semiconductive properties similar to those of Si, Ge, and GaAs materials. An 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 [Sze] for photovoltaic materials. This indicates that one should be able to use uranium oxides to make efficient solar cells. The electrical conductivity of intrinsic UO_2, as shown in Fig. 1, is approximately the same as GaAs and Si [Sze]. The dielectric constant of UO_2 (~22) is nearly double that for Si (11.2) and GaAs (14.1) [Samsonov], perhaps making UO_2 an attractive material for active electronic devices. The ceramic oxides of uranium, e.g. U_3O_8 or UO_2, can also withstand much higher operating temperatures: for example, the melting point of UO_2 is 2878°C.

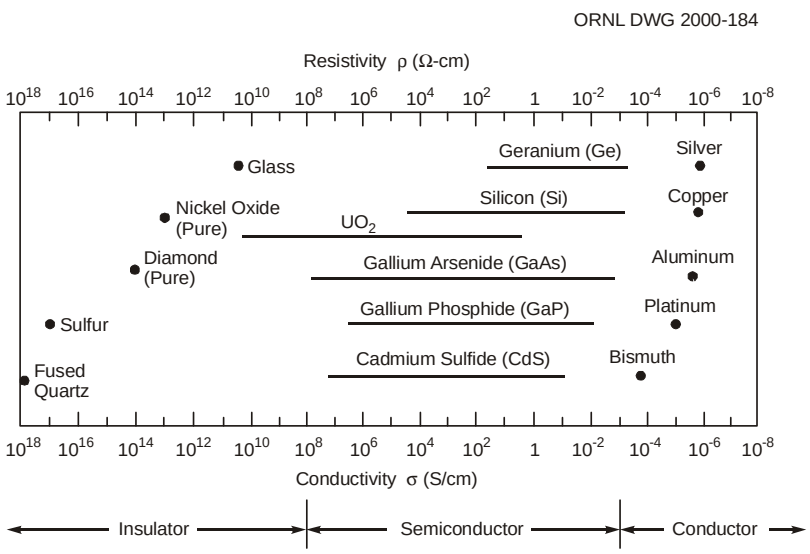

Fig. 1. Comparison of UO_2 Conductivity to Typical Range of Conductivities for Insulators, Semiconductors, and Conductors [Sze 1985].

Samples of polycrystalline UO_2 were ion implanted with various dopants to study their effect on its electronic properties. It is important to investigate how the electrical conductivity of UO_2 (urania) is affected by the introduction of impurity atoms in the form of solid solutions in order to pursue the use of urania in active components such as solar cells, thermophotvoltaics (TPV), diodes, and transisters. Literature reports that one bandgap for UO_2 is 1.3 ev and its dielectric constant is 22 [Samsonov]. Based primarily on this information, the following dopants were selected for study: S, Te, Al, P, B, and Sb. Literature only reports on the affect of CaO and

Nb_2O_5 dopants on the electrical conductivity of UO_2 [Belle] [Kileen]. One slightly increases the electrical conductivity (σ) of urania while the other decreases σ. Doses ranged from 8×10^{11} to 5×10^{16} atoms/cm^2. Atom concentrations ranged from 10^{17} to 10^{21} atoms/cc. Work done by Bates et al. [Bates], shown in Fig. 2 indicates the intrinsic conductivity of a single crystal of UO_2 is ~1.5 x 10^{-03} ohm^{-1}cm^{-1} at room temperature.

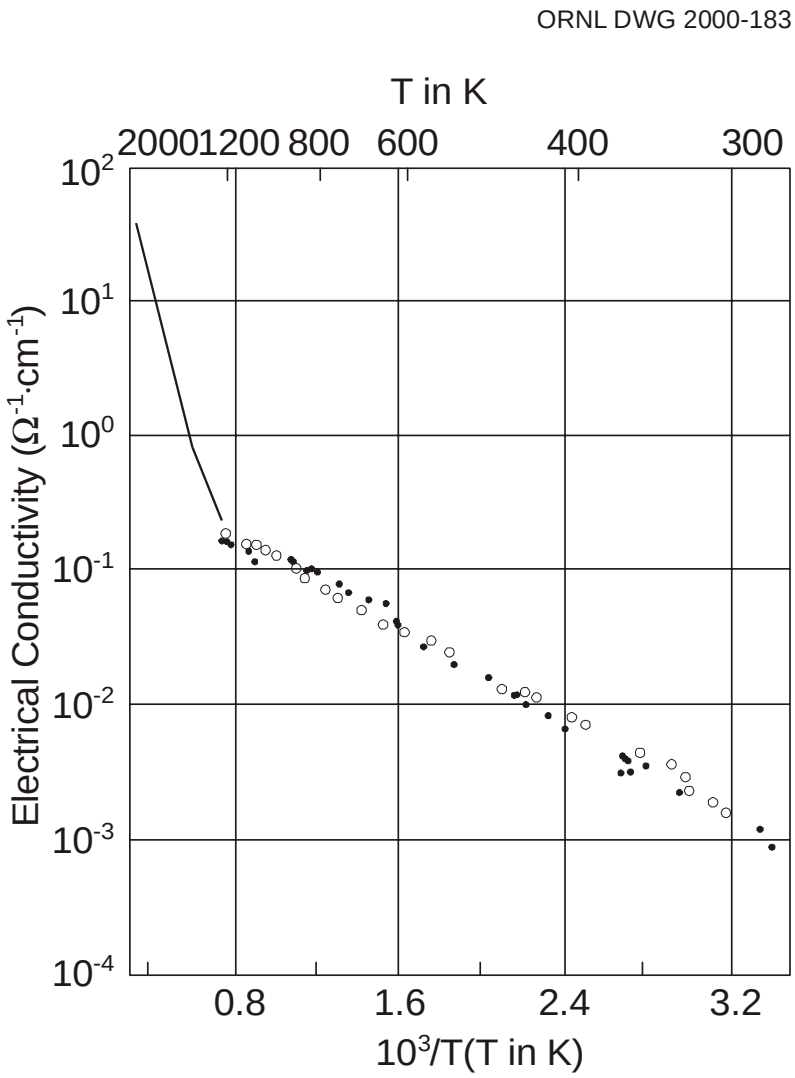

Fig. 2. The Electrical Conductivity of UO_2 Single Crystals as a Function of Temperature [Gmelin 1979].

2. SAMPLE PREPARATION, ION IMPLANTATION, AND CHARACTERIZATION

Samples were prepared in a hood by cutting sintered UO_2 pellets into either disks or rectangular geometries. Disk sample sizes were 0.635 cm outside diameter by either 0.317 or 0.158 cm thick while rectangular samples were 1.25 × 0.635 cm by either 0.317 or 0.158 cm thick. Samples were cut using a Buehler low-speed isomet saw with a diamond blade. Each sample was hand polished using 600 grit SiC paper and placed in a sealed glass container that contained anhydrous calcium sulfate (Drierite) dissicant pellets to reduce the moisture content.

Ion implantation of the samples was then carried out at the Ion Beam Laboratory at Los Alamos National Laboratory. The dopants were introduced into the electric field as chloride ions. Table 1 gives the deposition parameters.

Table 1. Deposition Parameters for Depleted Urania Samples

Ion energy kev	Dopant	Deposition depth (Å)	Dopant concentration at/cc	Dose at/cm^2
140	B	2097	10^{17}	4.47×10^{12}
			10^{19}	4.47×10^{14}
			10^{21}	4.47×10^{16}
150	Al	1050	10^{17}	2.75×10^{12}
			10^{19}	2.75×10^{14}
			10^{21}	2.75×10^{16}
150	P	900	10^{17}	4.03×10^{12}
			10^{19}	4.03×10^{14}
			10^{21}	4.03×10^{16}
300	S	1632	10^{17}	3.27×10^{12}
			10^{19}	3.27×10^{14}
			10^{21}	3.27×10^{16}
150	Te	528	10^{17}	5.63×10^{11}
			10^{19}	5.63×10^{13}
			10^{21}	5.63×10^{15}
150	Sb	537	10^{17}	5.8×10^{11}
			10^{19}	5.8×10^{13}
			10^{21}	5.8×10^{15}

After the samples were implanted, they were returned to Oak Ridge National Laboratory where they were characterized using the van der Pauw four point probe technique. Sample electrical resistivity was measured as a function of implantation dose.

3. DISCUSSION OF RESULTS

The electrical conductivity of intrinsic single crystal UO_2 is ~1.5 x 10^{-03} $ohm^{-1}cm^{-1}$ (667 ohm-cm) at room temperature [Bates et al]. The effect of doping UO_2 with impurities is shown in both Table 2 and Fig. 3. As can be seen from the data, the average electrical resistivity and the calculated electrical resistivity of the doped region decreases as a function of increasing dopant concentration. While some elements do not show much affect on the electrical resistivity, others such as Te and Al cause a marked decrease in electrical resistivity as a function of increasing concentration. The average resistivity (ρ_{avg}) shown in Column 4 of Table 2 was measured by the van der Pauw four-point probe technique. The model to evaluate parallel resistors in an electrical circuit,

$$R_{avg} = R_1 R_2 / (R_1 + R_2), \qquad [1]$$

was used to calculate the resistivity of the doped region. R_1 is the resistance of the doped region while R_2 is the resistance of the bulk region of the sample.

Resistivity can then be expressed as

$$(\rho_{avg}) = \left[\frac{(\rho_1 t_1 / A_1)(\rho_2 t_2 / A_2)}{(\rho_1 t_1 / A_1) + (\rho_2 t_2 / A_2)} \right] \frac{A}{t} \qquad [2]$$

where

$$R_1 = \rho_1 t_1 / A_1, R_2 = \rho_2 t_2 / A_2 \text{ and } R_{avg} = \frac{\rho_{avg} t}{A} \qquad [3]$$

The thickness and width of doped and undoped regions are given as t_1, t_2, and d, respectively. The cross sectional area of the doped region is $t_1 d$, while the cross sectional area of the undoped region is $t_2 d$. The sample total thickness is t and the sample total cross-sectional area is td.

As mentioned earlier, the average resistivity, (ρ_{avg}), as measured by the van der Pauw four-point probe technique, and, ρ_2, the resistivity of intrinsic single crystal urania as reported by Bates et al. to be 667 ohm cm are used to calculate the resistivity of the implanted region ρ_1 which is ρ_{dr} (resistivity of the doped region). Solving Eq. 2 for ρ_1 yields the data listed in column five of Table 2. The electrical conductivity listed in column six is simply the reciprocal of the data given in column five.

Table 2. Electrical Resistivity of Doped Urania Polycrystalline and Crystalline Samples

Sample no.	Dopant	Dopant Concentration (atoms/cc)	Measured Resistivity ρ_{avg} (Ω-cm)	Calc. Doped Resistivity ρ_{dr} (Ω-cm)	Calc. Doped Elec. Conductivity σ_{dr} (S/cm)
Undoped single crystal			667		1.5×10^{-3}
1a	B	10^{17}	323	0.146	6.85
2a	B	10^{19}	475	0.17	5.88
3a	B	10^{21}	450	0.067	14.9
4a	S	10^{17}	329	0.088	11.38
5a	S	10^{19}	321	0.092	10.91
6a	S	10^{21}	317	0.09	11.15
7a	P	10^{17}	521	0.143	7.0
8a	P	10^{19}	395	0.046	22.0
9a	P	10^{21}	398	0.081	12.3
10a	Al	10^{17}	549	3.1	0.32
11a	Al	10^{19}	690	103	0.097
12a	Al	10^{21}	174	0.117	8.55
13a	Te	10^{17}	822	182.67	0.0055
14a	Te	10^{19}	622	2.31	0.433
15a	Te	10^{21}	283	0.22	4.54
16a	Sb	10^{17}	271	0.323	3.1
17a	Sb	10^{19}	271	0.126	7.94
18a	Sb	10^{21}	251	0.096	10.47

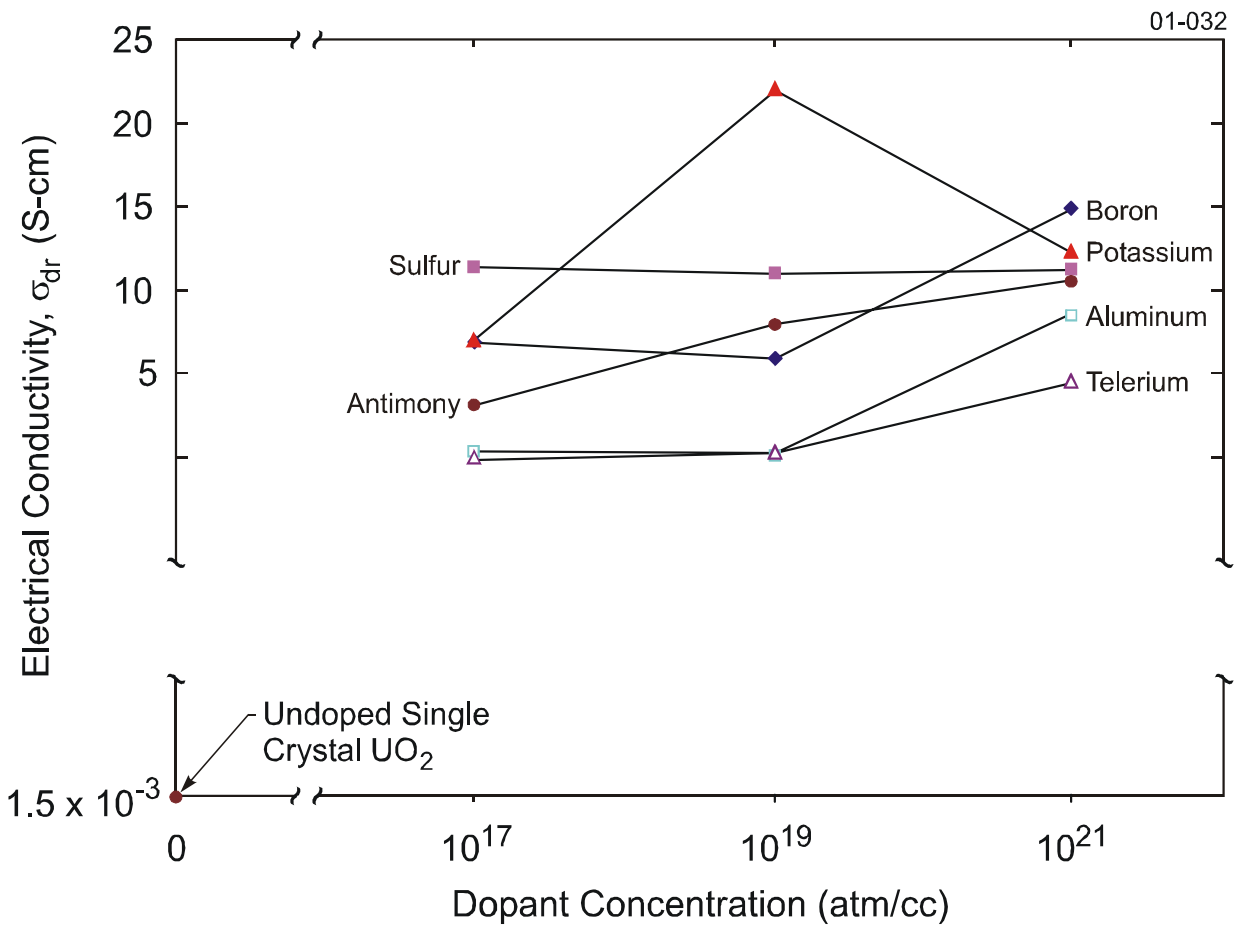

Fig. 3. Electrical Conductivity of Doped Polycrystalline UO_2 and Undoped Single Crystal UO_2 Samples.

If a parallel resistor model explains the electrical conductivity as a function of dopant concentration and dopant type in DUO_2, the electrical conductivity of DUO_2 can be increased by many orders of magnitude by doping DUO_2 with impurity atoms. If the parallel resistor model does not hold, then doping still influences the electrical conductivity of UO_2, however, to a lesser extent: the maximum effect shown by doping with aluminum at 10^{17} atoms/cc where the electrical conductivity is increased by 75% over the intrinsic case. Recent work (to be reported in a later paper) on the characterization of these samples by measuring dark current and light current seems to support the parallel resistor model.

4. CONCLUSION

It appears that the intrinsic electrical conductivity of UO_2 can be increased several orders of magnitude by ion implanting selected dopants. The level of change depends on dopant and dopant concentration.

ACKNOWLEDGMENT

This work was funded by the U.S. Department of Energy's Depleted Uranium Uses Research and Development Program.

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