SOME ELECTRICAL PROPERTIES OF ION-IMPLANTED URANIA — PART II

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ABSTRACT

As part of the U.S. Department of Energy's effort to evaluate the use of UO_2 as a material for photovoltaic (e.g., solar cell) applications [1], single-crystal UO_2 samples were characterized as to their electrical and electro-optical properties. Samples of UO_2 were ion implanted with boron and sulfur dopants as well as with boron and sulfur co-dopants at the Ion Beam Materials Laboratory facility at the Los Alamos National Laboratory. Activation energies for electrical conduction were measured to be from 0.13 to 0.26 eV, when temperatures varied from 180 to 450 K. Dark current was measured followed by light current under 1-sun illumination. In general, the dark and light currents were about an order of magnitude greater than those reported earlier for polycrystalline UO_2. Optical and infrared absorption and transmission data were also obtained and are reported. Transmission data on the single-crystal samples revealed a complex structure that made it difficult to resolve a single optical bandgap.

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KEY WORDS: Uranium Dioxide (UO_2), Semiconductors, Transport Properties

1. INTRODUCTION

Uranium is used as fuel for nuclear power plants and for weapons. However, little effort has been devoted to establishing other uses. The United States Department of Energy has initiated the Depleted Uranium Uses Research and Development Project to evaluate other potential beneficial uses of uranium [1]. As part of the Project's effort to evaluate photovoltaic (e.g., solar cell) applications, single-crystal UO_2 samples were characterized as to their electrical and electro-optical properties. Samples of UO_2 were ion implanted with various dopants at the Ion Beam Materials Laboratory facility at the Los Alamos National Laboratory. Substrates were either polycrystalline or single crystals of UO_2. Dopants used in this study are boron (B), silicon (S), and co-dopants of silicon and boron (S/B). Implantation energies ranged from 150 to 300 keV, and implantation depths ranged from a few hundred to over 2000 Å. Prior to testing, the samples were heated in vacuum at 350°C for several hours to ensure that the samples were not hyperstoichiometric. Activation energies for electrical conduction were determined by obtaining data on current vs. the reciprocal of temperature, where temperature was varied from 180 to 450 K. Activation energies were in the range of 0.13 to 0.26 eV. Samples were also characterized as to their dark current and photocurrent. Electrical contact was made using silver paint. Contact strips were ~5 mm long and 1 mm apart, and a voltage bias from 0.5 to 20 Vdc was placed across the contacts. Dark current was measured followed by light current with the application of 1-sun illumination. Optical and infrared absorption and transmission data were also obtained. Haire [2] previously reported optical absorption characteristics of UO_2 implanted with tellurium and antimony. Killeen reported the effect of niobium on the electrical conductivity of UO_2 Killeen [3], and Bates et al. [4] investigated the intrinsic electrical conductivity of urania.

2. EXPERIMENTS

Table 1 provides deposition parameters for the dopants listed above. Single crystals doped with boron were also characterized. The single-crystal samples were grown by the arc fusion method. After implantation, these samples were heated at 350°C in vacuum to ensure that the samples were not hyperstoichiometric.

Table 1. Deposition Parameters for UO_2 Samples

Sample No.	Dopant	Energy (keV)	Dopant Deposition Depth (Å)	Dopant Concentration (at/cm^3)	Dopant Dose (at/cm^2)
23C	B	140	2237	10^{17}	4.47×10^{12}
24C	S/B	300/140	1630/2237	$10^{17}/10^{19}$	3.26×10^{12} /4.47×10^{14}
25C	S/B	300/140	1630/2237	$10^{19}/10^{21}$	3.26×10^{14} /4.47×10^{16}
26C	S	300	1630	10^{21}	3.26×10^{16}

Optical and infrared absorption and transmission data were obtained using a Cary 5G UV/visible/near-IR spectrophotometer. Data were collected over wavelengths ranging from 400 to 3300 nm. Dark current and photocurrent data were obtained on samples with a constant applied voltage of 5 Vdc. Thermal currents were measured over a temperature range of 180 to 450 K. Here the applied voltage varied from 0.52 to 0.73 Vdc.

For electrical measurements, samples were contacted by using spring-loaded probes that were pressed onto silver-painted strips approximately 4 mm long by 1 mm wide separated by a distance of approximately 1 mm. Illumination intensity in all cases was approximately 1 sun.

3. RESULTS AND DISCUSSION

The first objective of the optical transmission experiment was to determine the bandgap of single-crystal UO_2 . The grayish matte appearance of the sample indicated that significant light scattering occurs, suggesting that an integrating sphere model should be used in interpreting the data. Figure 1 shows the integrated transmission and reflection data for this approximately 100-µm-thick sample. Fig. 1 suggests that UO_2 has a very unusual structured absorption edge not seen in other semiconductors. Previous work [5], perhaps arbitrarily, identified the shoulders seen in Figs. 1 and 2 near 900, 1100, 1800, 2500, or 3100 nm as single "bandgaps." However, it does not appear logical to define a UO_2 bandgap in terms of a single wavelength (energy) value.

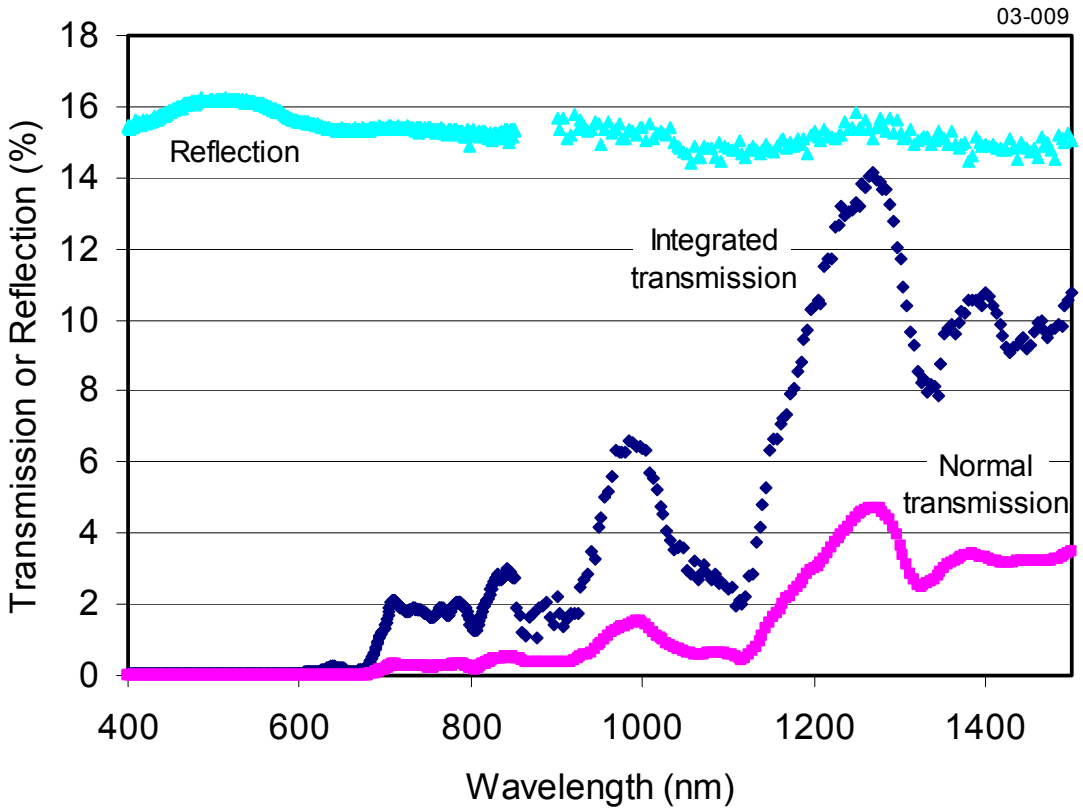

Fig. 1. Absorption peaks for single-crystal UO_2.

Next, optical transmission experiments of doped polycrystalline UO_2 samples were conducted. There was insufficient light transmission below 2000 nm in these samples to determine absorption coefficients. We extended the measured wavelength range to 3300 nm. However, the integrating sphere could no longer be used in this range. Figure 2 shows the normal transmission for the same single-crystal sample of Fig. 1 and a doped polycrystalline sample that was essentially opaque for wavelengths below 2500 nm. Given the sample thickness, the transmission values in Fig. 2 correspond to absorption coefficients (α) ranging from ~100 to 1000 cm^{-1}. In many semiconductors, the bandgap occurs for energies when the absorption coefficient reaches approximately $\alpha \approx 100$ cm^{-1} for indirect bandgap materials and $\alpha \approx 1000$ cm^{-1} for direct bandgaps. In UO_2 there is so much structure in the strongly absorbing transitions which makes it impossible to define a bandgap by a single energy.

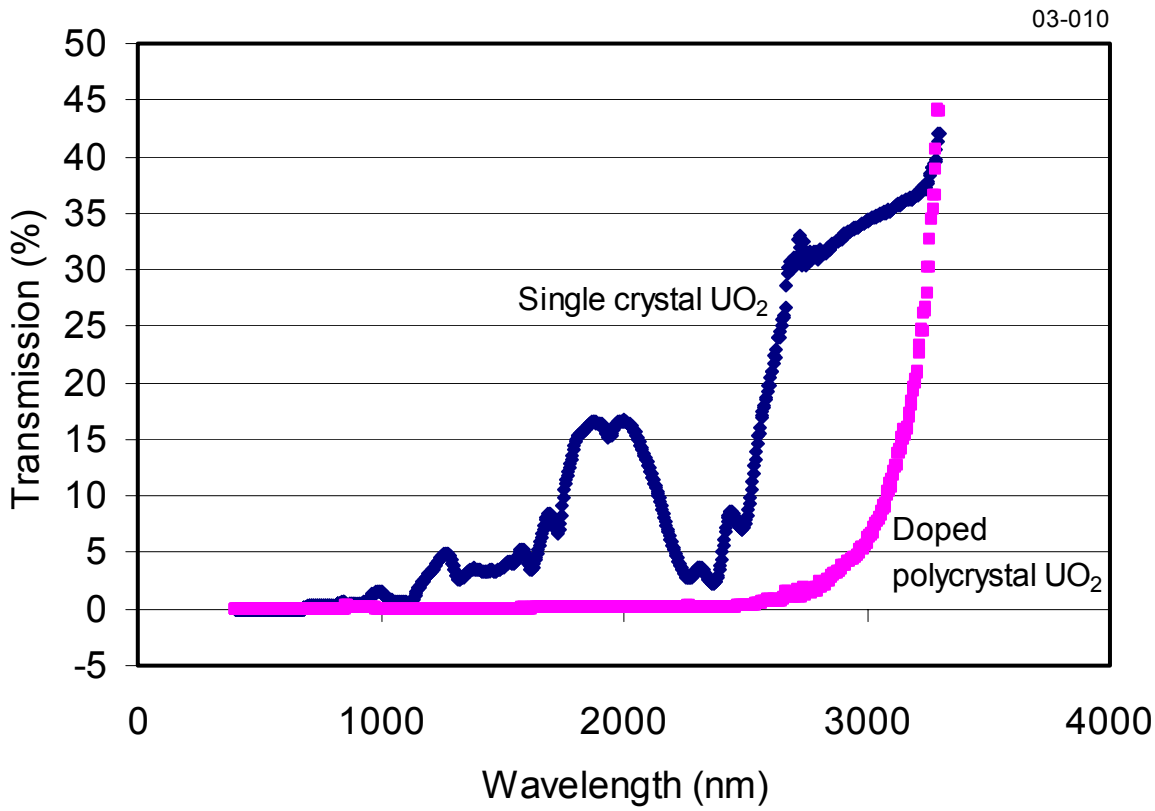

Fig. 2. UO_2 transmission data for determination of absorption coefficients.

The activation energy for conduction for each of the dopants was determined by measuring current as a function of inverse temperature, as shown in Fig 3. For an undoped single crystal (sample #16C), the activation energy for conduction is 0.26 eV. For a single crystal doped with boron (sample # 23C), the activation energy for conduction is 0.14 eV. Co-doping with sulfur and boron (samples # 24C and 25C) gave an activation energy of 0.26 eV for sample 24C (10^{17} at/cm^3 of boron and 10^{19} at/ cm^3 of sulfur) and 0.17 eV for sample 25C (10^{19} at/ cm^3 of boron and 10^{21} at/ cm^3 of sulfur). We find that sulfur doping by itself is quite efficient and that co-doping reduces, rather than enhances, conductivity. Also included in this figure are the data for an undoped UO_2 sample. The low temperature currents and the high temperature currents do not coincide because the low temperature data was taken with 5 V applied to the contacts, while the high temperature data was taken with 0.72 V applied.

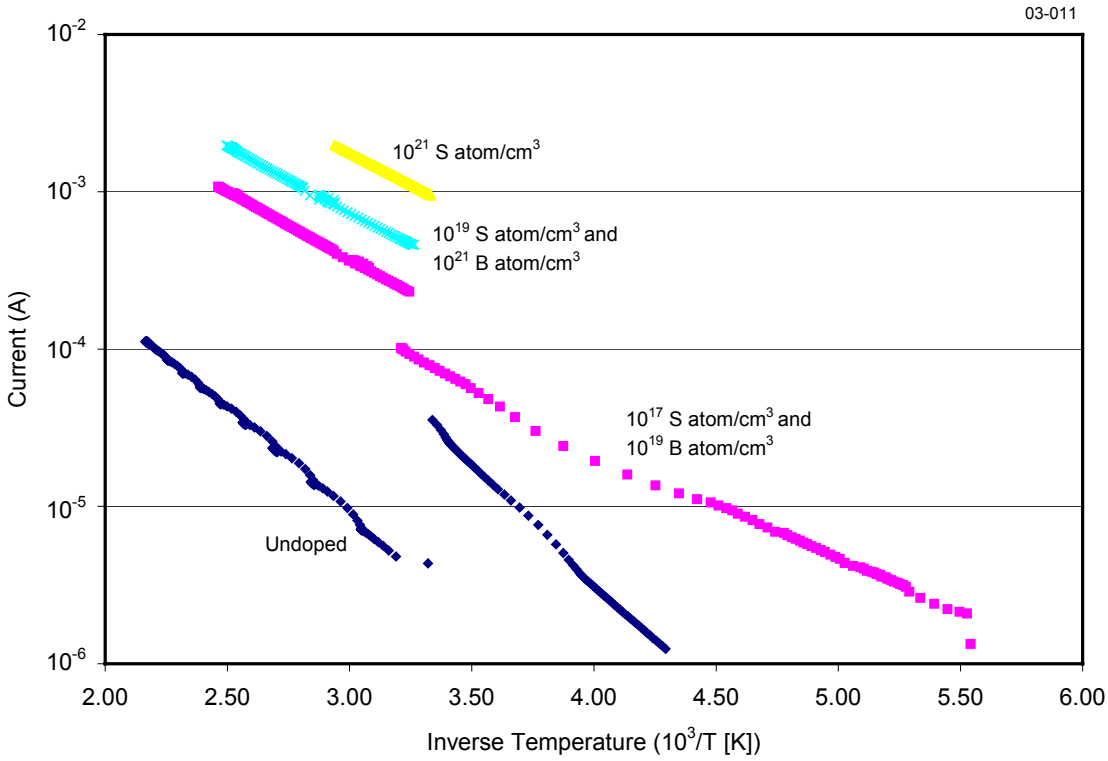

Fig. 3. Determination of UO_2 activation energy for electrical conductivity.

Light and dark currents were measured when doped UO_2 samples were illuminated under 1-sun intensity, as in earlier experiments [2]. Figure 4 shows dark current, I_d, and light current, I_L, for a single crystal of UO_2 doped with 10^{17} at/ cm^3 of boron. A peak I_d of 7.9 mA occurred after 180 s, followed by a peak I_L of 9 mA after 210 s. Figure 5 shows I_d and I_L as a function of time for single-crystal urania doped with 10^{21} at/cm^3 of sulfur. Peak I_d occurred after 660 s, and a peak I_L of 12.7 mA occurred after the sample was illuminated for 1300 s.

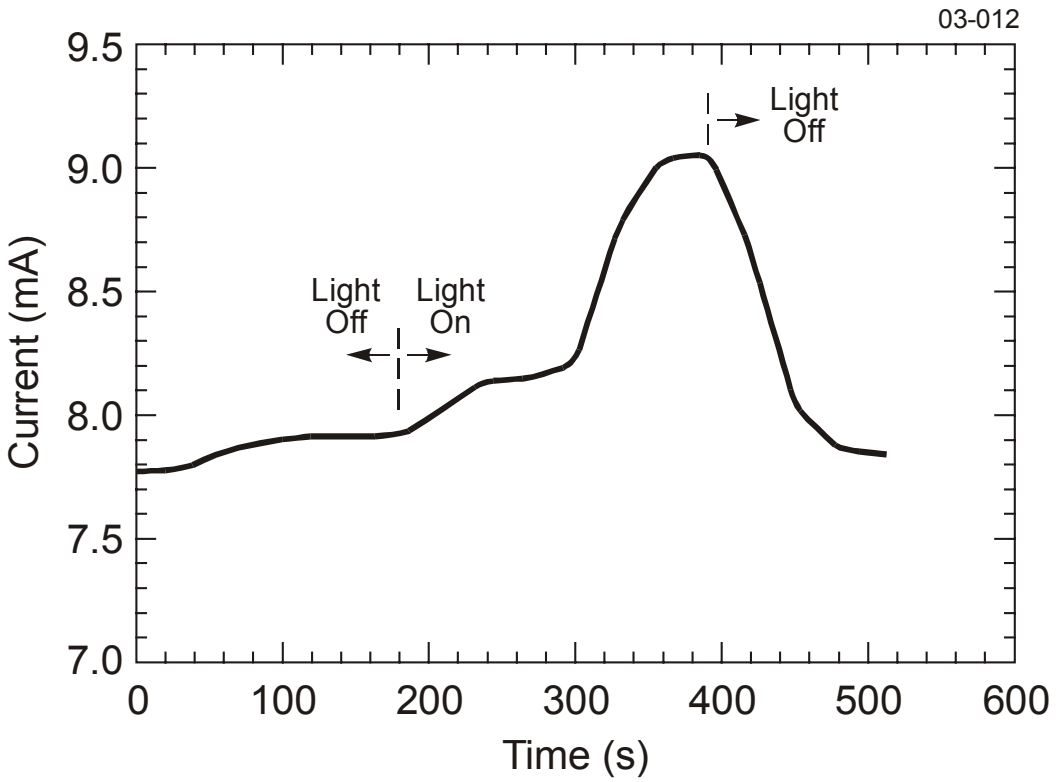

Fig 4. Boron-doped (10^{17} B atom/cm^3) UO_2 response to illumination.

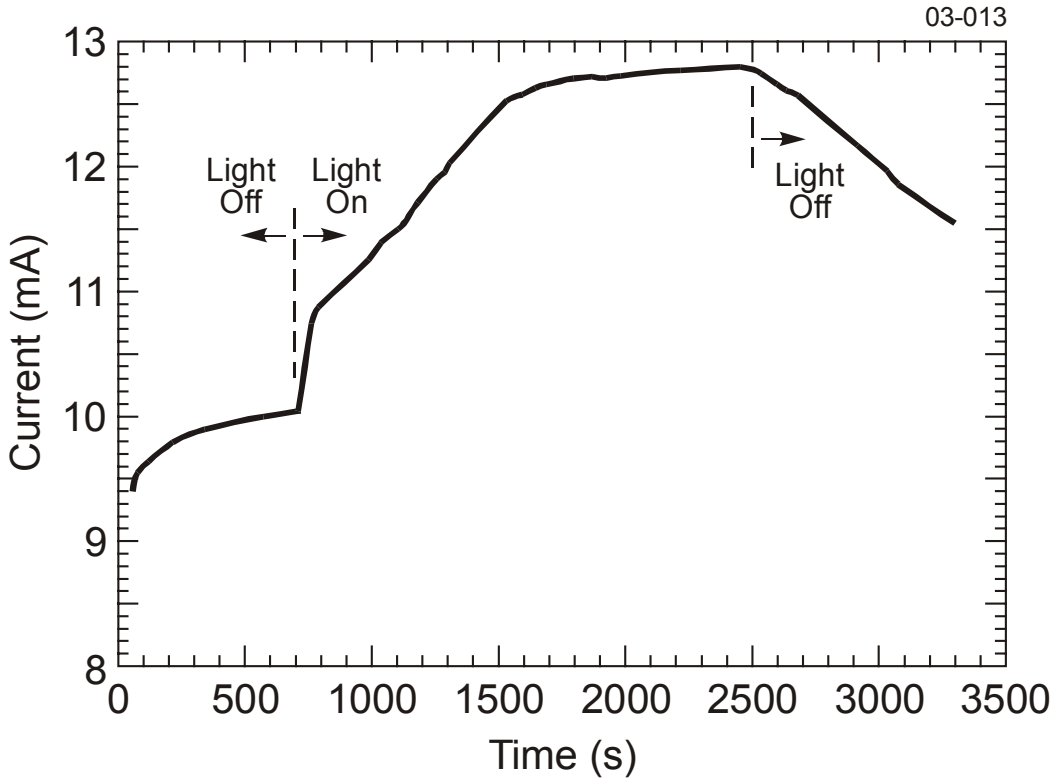

Fig 5. Sulfur-doped (10^{21} S atom/cm^3) UO_2 response to illumination.

Figure 6 shows two single-crystal UO_2 samples co-doped with sulfur and boron at concentrations of (1) 10^{17} at/ cm^3 (B) and 10^{19} at/cm^3 (S) and (2) 10^{19} at/ cm^3 (B) and 10^{21} at/cm^3 (S). For the former sample, a peak I_d of 3.3 mA occurred after 210 s while a peak I_d of 6.1 mA occurred after 1590 s of illumination under 1-sun conditions. For the latter sample, a peak, I_d of 6.4 mA occurred after 180 s and a peak I_L, of 8.4 mA occurred after 2300 s of illumination. Figure 7 compares the dark and light currents for all of the samples discussed above. The interpretation of the temperature, time, and light-dependent currents is not straightforward. It is difficult to separate the effects of light, heating, electric-field- and time-dependent changes. Nonohmic and time dependent transport phenomena have no been observed for most single and polycrystalline UO_2 samples. Such behavior is very rarely noted in other semiconductors or transparent conductive oxides (TCOs). It is remarkable, however, that each sample undergoing the same measurement sequence shows differences in the time dependence of the currents, suggesting a qualitatively similar transport mechanism for carriers with quantitative sample-to-sample differences.

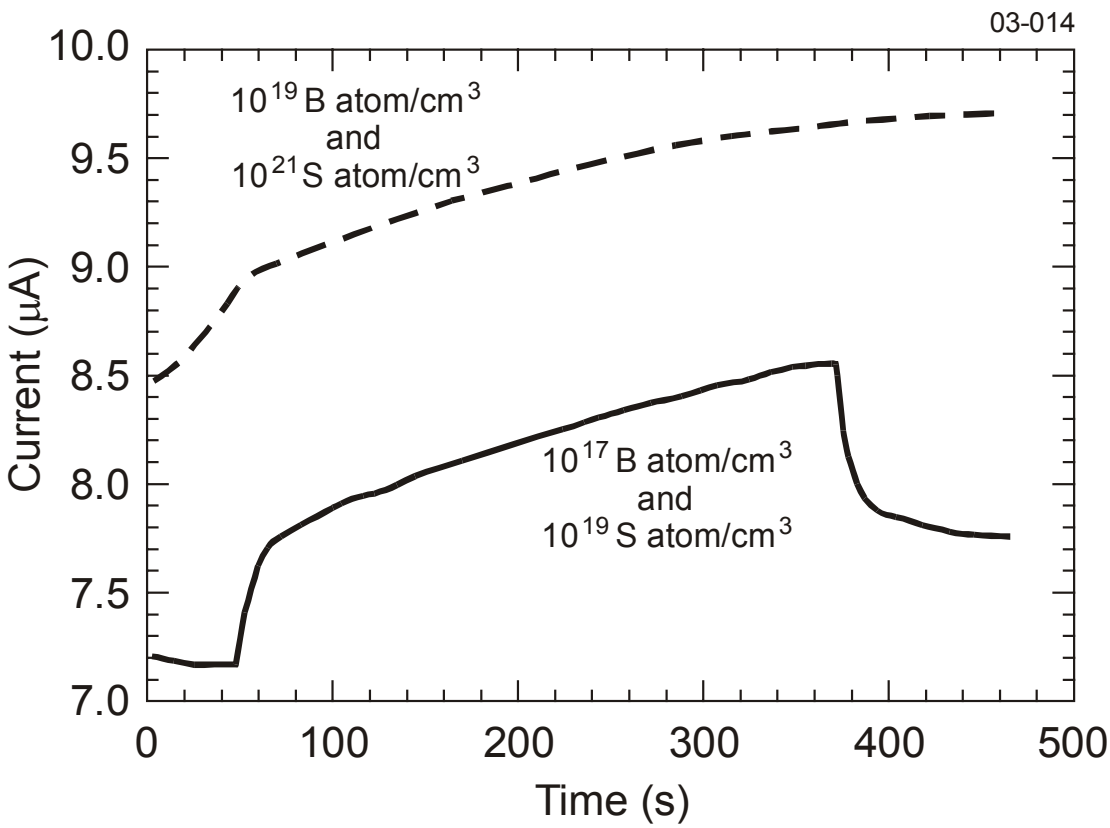

Fig. 6. Co-doped single-crystal UO_2 response to illumination.

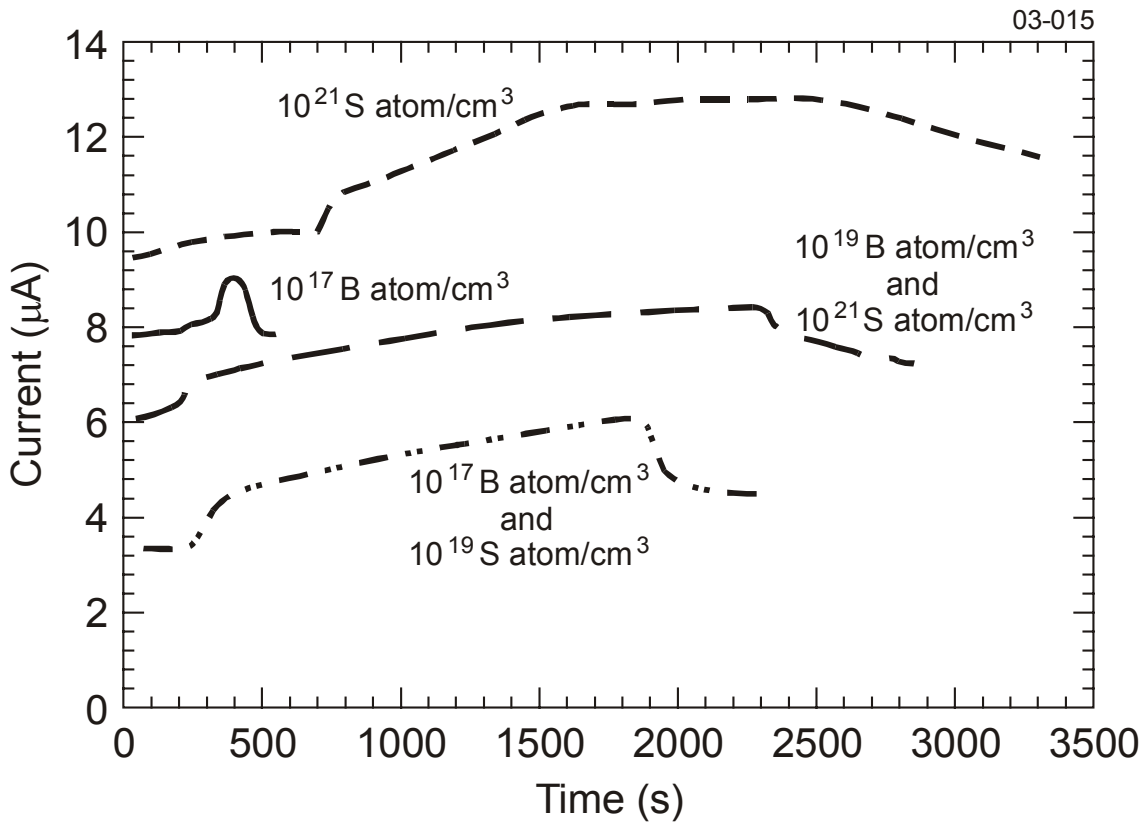

Fig. 7. Comparison of dark and light currents for all samples.

The optical transmission data indicate that strong absorption occurs in the infrared region and that a very unusual and structured absorption edge occurs for shorter wavelengths. Many absorption peaks have been observed in the infrared radiation spectrum [6] and are consistent with our observations. Absorption peaks also occurred in the visible range of the radiation spectrum and for corresponding absorption coefficients of several 100 cm^{-1}. In the visible range, the absorption is strong enough to be determined by band-to-band transitions. This is a unique behavior that has not been observed in any other semiconductor or TCO system. Further studies of thin-film UO_2 samples may allow a better quantitative correlation between the electrical transport behavior and the joint density of states determined by absorption. For UO_2, a simple bandgap cannot be defined because the absorption increases in the visible/near-IR range are too shallow and too structured. However, our data suggest that somewhere between 0.4 and 1.3 eV, a transition from localized to extended states [7] may occur. The electrical transport properties could be determined by carriers transitioning between the observed peaks in the joint density of states. Furthermore, all UO_2 samples measured to date exhibited p-type (hole-dominated) transport as determined by thermoprobe experiments. On a few selected samples, we checked for the magnitude of the photoconductivity while the samples were cooled to 180–200 K.

Interestingly, even at these low temperatures, when the room-temperature currents were reduced by approximately four orders of magnitude, the illumination did not significantly enhance the photocurrents. While we know that the light is being absorbed, the resulting excess carriers do not appear to significantly alter the dark carrier densities (or distributions) to cause appreciable changes in current flow.

4. CONCLUSIONS

Doping single-crystal UO_2 can markedly affect its electrical conductivity and photoconductivity. However, we were not able to establish a systematic predictable response of the conductivity values to the doses and atomic species implanted. Dark currents and photocurrents measured in single-crystal UO_2 are approximately one order of magnitude greater than those measured in polycrystalline UO_2, as reported in earlier work [8]. Co-doping of UO_2 with both boron or sulfur resulted in photocurrents less than those for the samples singly doped with boron and sulfur. Nonohmic conduction in UO_2 is also a very unusual behavior. Nonohmic conduction is normally seen only under extreme (very high applied electric field) operating conditions such as "avalanching." Optical and infrared transmission results reveal a very unusually structured "shallow" absorption edge not seen in other semiconductors or TCOs. The magnitude of the thermoelectric signal always indicates p-type material and is remarkably insensitive to the implanted dopant levels, species, and conductivity levels.

5. ACKNOWLEDGEMENT

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