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The Effect of Co-Doping on the Photoelectric Properties of UO_2

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INTRODUCTION

As part of the U.S. Department of Energy's effort to evaluate the use of UO_2 as a material for semiconductive applications,^{1,2} single crystals of UO_2 were co-doped. Single-crystal UO_2 samples were ion implanted with various concentrations of oxygen followed by secondary doping with Te, P, Sb, or N.

The single-crystal samples were prepared at the Ion Beam Materials Laboratory facility at the Los Alamos National Laboratory. Dark current and photocurrent data were obtained on samples with a constant applied voltage of 5 Vdc. The samples were contacted by using spring-loaded probes that were pressed onto silver-painted strips ~4 mm long by 1 mm wide separated by a distance of ~1 mm. Illumination intensity in all cases was ~1 sun. The samples were then characterized as to their electro-optical properties.

RESULTS AND DISCUSSION

Co-doping of semiconductors generally results in lower carrier mobility and conductivity (i.e., lower photocurrents).³ However, in a few instances, co-dopants increase carrier mobility and conductivity. Such phenomena are reported herein.

Another remarkable result described in the literature is that co-doping can cause n-type ZnO to become p-type material. Hitherto, ZnO could only be doped n-type. Yamanoto and Katayama-Yoshida⁴ first demonstrated the influence of co-doping on semiconductive properties. In the experimental work by Joseph et al.,⁵ n-type ZnO was converted into

p-type through co-doping with N_2O and Ga. When Ga was not used, the ZnO remained n-type. It should be noted that for the preparation of p-type ZnO, an electron cyclotron resonance source was also used to create activated n species. The types of crystalline defects formed and their concentrations determined whether p-type conduction was observed. In ZnO, the relevant defects are substitutional N atoms at an oxygen site, N_O , and substitutional N_2 at an oxygen site, $(\text{N}_2)_\text{O}$. In ZnO, N_O is an acceptor while $(\text{N}_2)_\text{O}$ is a shallow donor. Thus, it is the relative concentrations of these two defects that determine the doping type. It was determined that oxygen vacancies and hydrogen have a secondary role in conduction in the ZnO system. Yan and Zhang⁶ have predicted that doping with either NO or NO_2 would make ZnO p-type while doping with N_2 or N_2O would make ZnO n-type. As a result of research in growing epitaxial films, Yan and Zhang suggest that Ga serves to deplete the nitrogen so that NO molecules survive and reach the growing surface instead of being reconverted to N_2O .

Based on these results with ZnO, p-type UO_2 was co-doped with oxygen and other elements to determine if UO_2 could be converted from p-type into n-type material.

Table I and Figure 1 summarize the results of this work. As shown in Table I, in all cases except for those involving nitrogen, co-doping results in a marked decrease in photocurrent when compared with the use of single dopants alone. For co-doped nitrogen in single crystals (sample numbers 18C* and 23C*), light and dark currents are approximately an order of magnitude greater than those observed for

polycrystalline samples. For co-doping with 1.65×10^{22} at/cc of oxygen and 10^{21} at/cc of nitrogen, Figure 1 shows a photocurrent of 12 mA. This photocurrent is as large as any that we have observed for our singly doped samples (e.g., aluminum).

Our data show that the effect of reducing the interstitial concentration of oxygen by ~10% causes a reduction in light current of ~33%. This suggests that interstitial oxygen, in conjunction with nitrogen, resides on oxygen sites and plays a role in current conduction in UO_2 . More work is needed to further identify the interactions that take place between nitrogen and interstitial oxygen in the conduction process.

We have not yet demonstrated convincingly that true co-doping exists in UO_2 . Although no conclusive proof such as carrier n- or p-type inversion or much higher/lower conductivity has been established, our findings suggest that a co-doping mechanism could exist in UO_2 . Our experiments have shown that certain combinations of dopants increase the conductivity while other combinations decrease it. It is not yet clear whether co-doping can convert p-type UO_2 to become n-type material.

SUMMARY AND CONCLUSIONS

Photocurrents of single UO_2 crystals are as much as an order or magnitude higher than those reported earlier for polycrystalline materials and three orders of magnitude greater than those for intrinsic UO_2 .²

Co-doping UO_2 single crystals with oxygen and nitrogen causes higher dark and light currents than those produced via singly doping with oxygen or nitrogen alone. As seen in Figure 1, when oxygen and nitrogen are co-doped, the photocurrent is the highest that we have measured with UO_2 (12 mA). However, co-doping UO_2 with oxygen and Te, Sb, or P has the opposite effect of reducing the observed dark and light currents.

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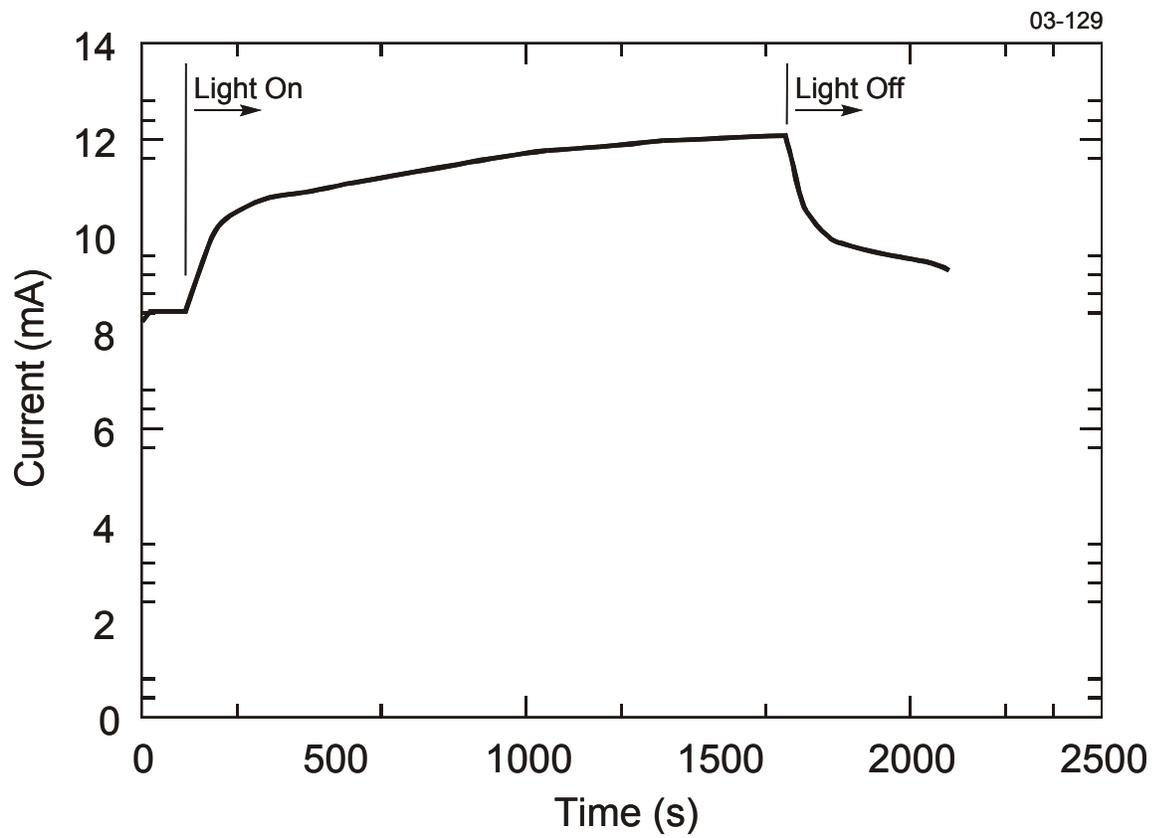


Fig. 1. Dark and light current for UO_2 co-doped with 1.65×10^{22} at/cm of oxygen and 10^{21} at/cc of nitrogen.

Table I. Deposition Parameters for UO₂ Samples

Sample no.	Dopant	Energy (keV)	Deposition Depth (D)	Dopant conc. (at/cm³)	Dose (at/cm²)	Dark/light current (mA)
19C*	O/Te	150/300	1471/528	$1.65 \times 10^{22}/10^{21}$	$5.66 \times 10^{17}/9.5 \times 10^{15}$	2.7/3.1
21C*	O/P	150/150	1471/880	$1.65 \times 10^{22}/10^{19}$	$5.66 \times 10^{17}/2.342 \times 10^{16}$	2.0/2.3
27C*	O/Sb	150/300	1471/537	$1.245 \times 10^{22}/10^{21}$	$4.262 \times 10^{17}/9.8 \times 10^{15}$	2.5/3.3
18C*	O/N	150/150	1471/1636	$1.65 \times 10^{22}/10^{21}$	$5.66 \times 10^{17}/4.37 \times 10^{16}$	8.4/12.0#
23C*	O/N	150/150	1471/1636	$1.488 \times 10^{22}/10^{21}$	$5.095 \times 10^{17}/4.37 \times 10^{16}$	5.6/8.8
24C*	O/Te	150/300	1471/528	$1.488 \times 10^{22}/10^{21}$	$5.095 \times 10^{17}/9.5 \times 10^{15}$	3.5/5.6
25C*	O/Sb	150/300	1471/537	$1.488 \times 10^{22}/10^{21}$	$5.095 \times 10^{17}/9.8 \times 10^{15}$	4.44/7.0
1C*	O	150	1471	2.62×10^{21}	8.898×10^{16}	7.2/11.61
32C	N	150	1636	10^{21}	4.3×10^{16}	4.08/4.56
16C*	Intrinsic	0	0	0	0	0.015/0.057
20C (Ref. 7)	Te	300	528	10^{21}	9.5×10^{15}	7.0/8.8
Polycr. (Ref. 6)	Te	300	528	10^{21}	9.5×10^{15}	0.8/1.4
3C*	P	150	880	10^{19}	2.34×10^{12}	2.92/4.0
Polycr. (Ref. 8)	P	150	880	10^{17}	2.342×10^{12}	0.23/0.47
1C	Sb	300	537	10^{21}	9.8×10^{15}	3.35/3.89
Polycr.	Sb	300	537	10^{21}	9.8×10^{15}	0.33/0.58

All data are for single-crystal samples at 5-Vdc bias, except where noted by pound sign (#). For sample 18C*, the voltage bias is reduced from 5 to 4 Vdc due to saturation effects.