

AD-A182 919

SUPERIONIC CONDUCTOR REPETITIVE OPENING SWITCHES FOR
ADVANCED PULSE POWER(U) COLORADO UNIV AT BOULDER
J F SCOTT 30 JUN 87 153-4785 N00014-86-K-0516

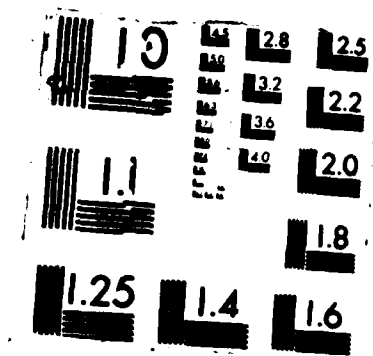
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The initial phase of investigation has been completed to analyze an unusual photoelectric effect in the superionic conductor silver iodide tungstate ($Ag_{13}I_9W_2O_8$). This material exhibits a sharp decrease in electrical conductivity upon illumination with laser light (in contrast to the increase observed for all other known materials), which suggests its potential use as a very fast, repetitive opening switch. Our work this year reveals a previously unknown aging process that may preclude commercial development of such an opening switch. This was independently discovered by Suthanthiraraj this year (Bull. Electrochem. 2, 553 (1986)). In the dark, the power drops by 84% after 125 days, when utilized as a battery; similar degradation occurs for use as a switch. The presence of laser light greatly accelerates the aging. A very fast all-operational-amplifier circuit has been designed and fabricated to measure optical response of this material; however, the need to use fresh samples for reproducible results complicates the program.			
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Annual report on ONR/SDIO award N00014-86-K-0516:

1) Instrumentation: We have designed and fabricated a fast circuit for measuring photoconductive effects with pulsed laser excitation. This circuit is diagrammed in Fig. 1 and uses op-amps entirely. It is significantly faster than the bridge circuits we used to measure this effect in our initial work (Ref. 1).

We also have made operational two pulsed laser systems for excitation; the first is a 1 MW excimer laser with pulse lengths of order 5 ns, and the second is a mode-locked dye pumped by a mode-locked Ar laser, emitting approximately 1 kW in 40 ps.

2) Student thesis generation: Three Ph.D. students in the Department of Physics have been supported in part by this grant this year. They are B. Melnick, J. Orrey, and D. Atkins. All are US citizens.

3) Publications: Abstracts of this work have been submitted for two conferences. The first is ILS-3 (International Laser Science Conference) in Atlantic City, Nov 1-5, 1987. Our paper (abstract attached) is scheduled for oral presentation as paper number 14-C. An abstract has also been submitted for a January 1988 conference on innovative technology in San Francisco. Both papers deal with accelerated aging in $\text{Ag}_{13}\text{I}_9\text{W}_2\text{O}_8$ under laser illumination.

4) Technical summary: When we began this study it was assumed that the material of interest ($\text{Ag}_{13}\text{I}_9\text{W}_2\text{O}_8$, sometimes erroneously still labelled as $\text{Ag}_6\text{I}_4\text{WO}_4$, as originally specified by Takahashi in Ref. 2) was stable. However, we discovered this year that it ages rapidly. This was independently discovered by Dr. S. A. Suthanthiraraj at Madras University in December 1986 (Ref. 3). His data show a degradation in peak discharge current from 1.6 microamps (3.5 microwatts) after 50 days in the dark to only 0.3 microamps (0.5 microwatts) after 125 days of storage. Our results show even more rapid aging when the specimen is exposed to laser light. We have been able to show that this arises from silver atoms plating out on the surface (see Fig. 2), presumably due to photovoltaic effects. While we are still measuring the magnitude and speed of the photoconductive changes in this material, we recognize that such measurements must be made on fresh samples. Therefore we have temporarily sidestepped the issue of speed to try to measure the aging effects quantitatively. Fig. 3 and 4 show photoconductive changes on two samples (each 90 days old) from Madras. Unfortunately, in each case the sign of the photoconductivity change with illumination is positive; approximately 10% increase with 1 W/cm^2 . This is opposite the effect we observed originally (Ref. 1). We believe that this is due not to aging, but to the fact that we are now using a pressed pellet that is poly-crystalline. Our original negative photoconductivity was observed only perpendicular to the C_2 axis of an oriented single crystal; it is quite possible that a positive effect occurs along the twofold axis, and that in a polycrystalline specimen the space-averaged effect is small and positive. Single crystals are being grown under pure oxygen (a technique previously successful -- Ref. 4) to test this hypothesis.

References:

- 1) F. Habbal, J. A. Zvirgzds, and J. F. Scott, Journal of Chemical Physics 69, 4984 (1978).
- 2) T. Takahashi, J. Electrochem. Soc. 120, 647 (1973).
- 3) S. A. Suthanthiraraj, Bull. Electrochemistry 2, 553 (1986).
- 4) S. Geller et al., Physical Review B21, 2506 (1980).

Figure captions:

- 1) Schematic diagram of the operational amplifier circuit used to measure rapid changes in photoconductivity due to pulsed laser illumination.
- 2) Photograph (x25 enlargement) of $\text{Ag}_{13}\text{I}_9\text{W}_{28}\text{O}_8$ under laser illumination, showing plating of neutral silver atoms at the surfaces along the C_2 -axis.
- 3) Voltage versus temperature across $\text{Ag}_{13}\text{I}_9\text{W}_{28}\text{O}_8$ specimen #20 with and without 1 W/cm^2 of blue light. The higher voltage corresponds to lower conductivity and is the dark value (circles); the squares are the illuminated voltage values.
- 4) As in Fig. 3, only for specimen #10, showing a smaller effect (approx. 5%), but of positive sign, as in Fig. 3.

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$$R_{\text{sample}} = \frac{V_{\text{ac}}}{V_{\text{out}}} (1\text{k}\Omega)$$

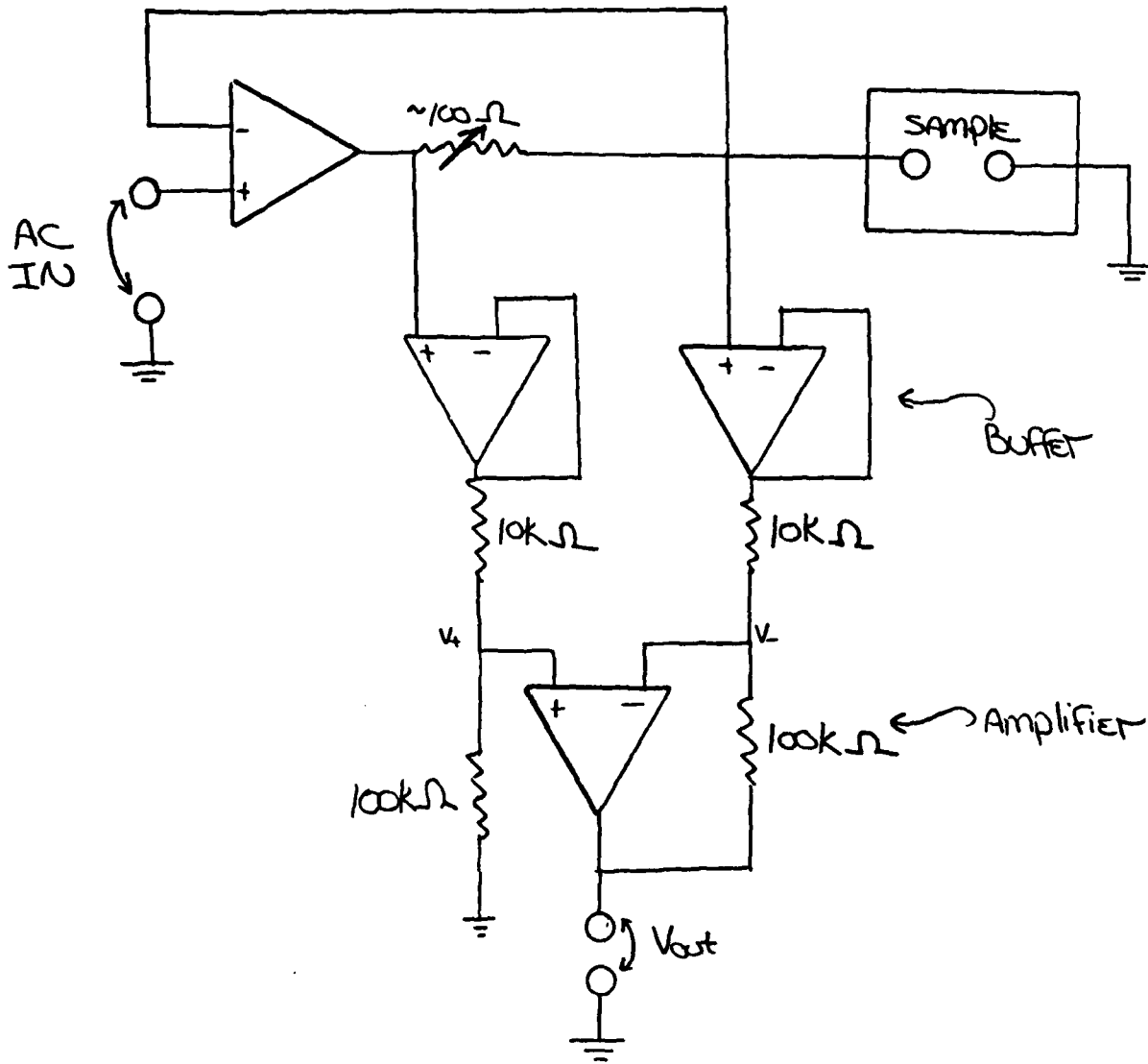
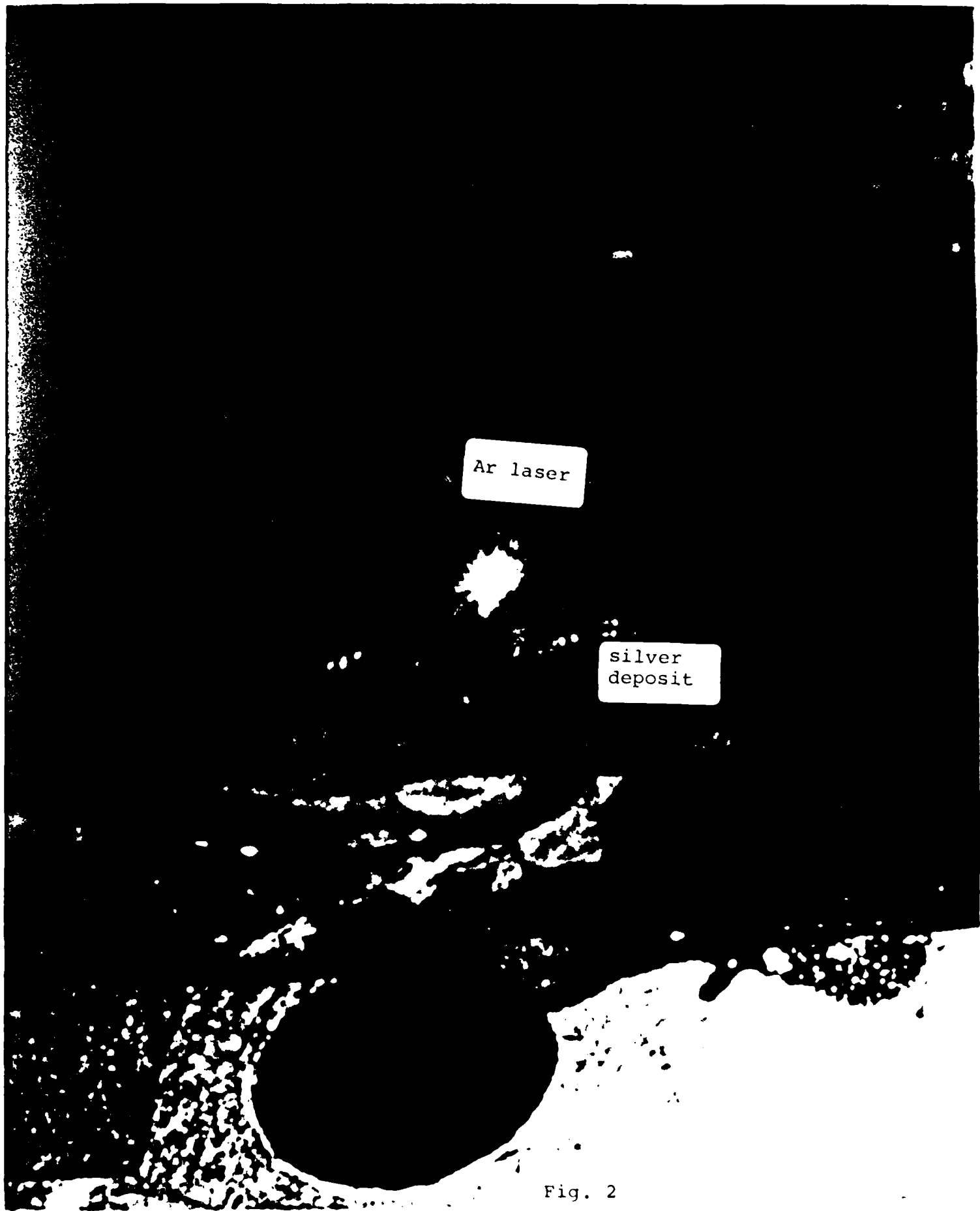


Fig. 1 All op-Amps ARE LF 356N



Ar laser

silver
deposit

Fig. 2

SAMPLE #20

8.50

TIME

6.00

2.57

TEMPERATURE

245

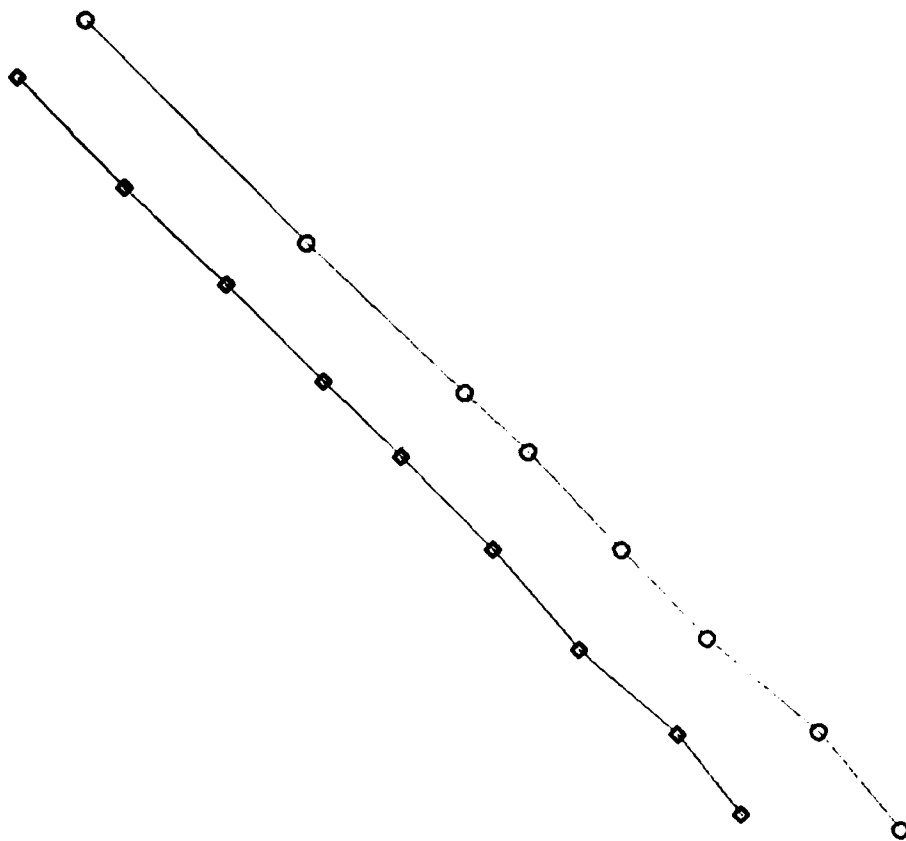


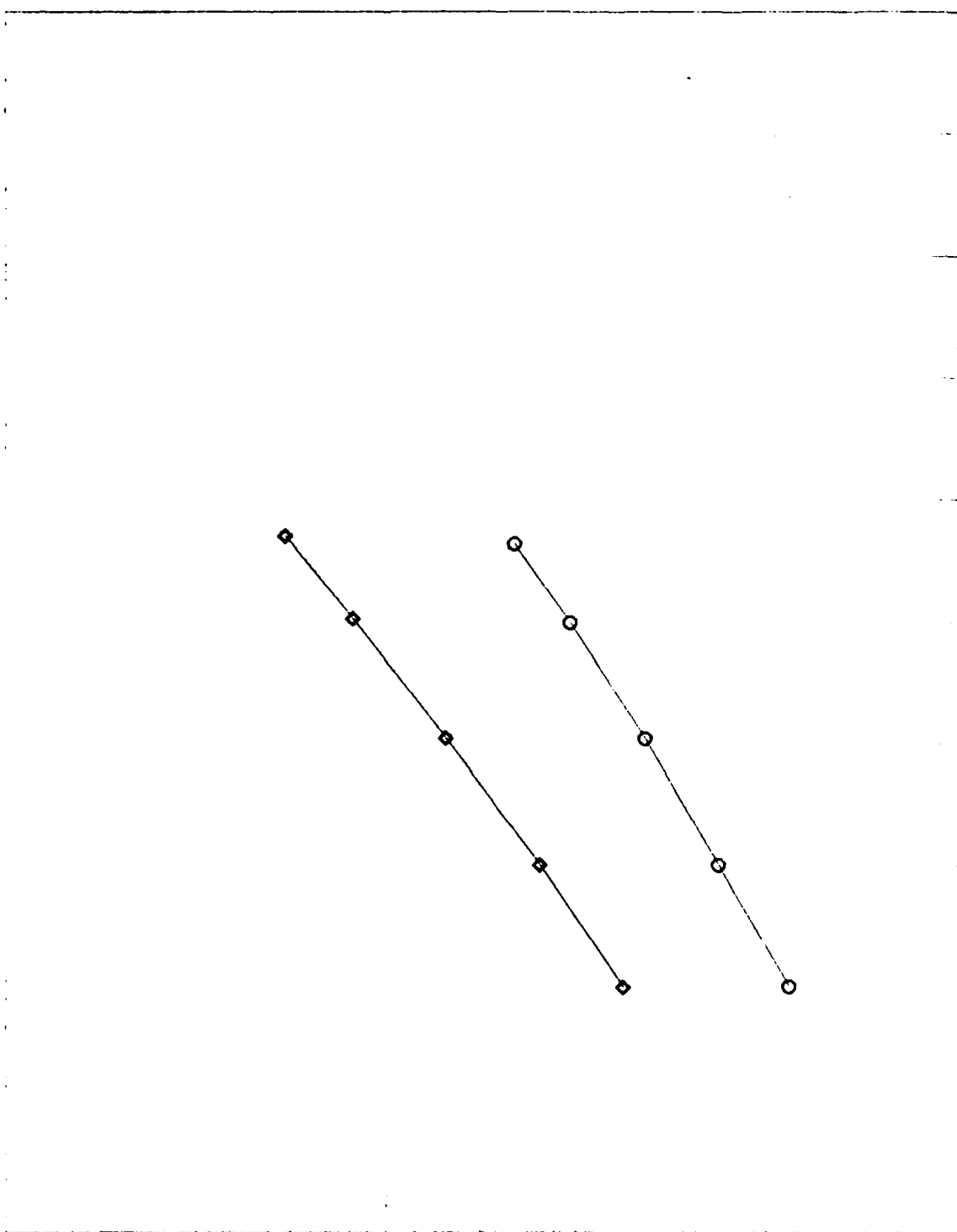
Fig. 3

SAMPLE #10

2.50

VOLTAGE

1.50



195.

TEMPERATURE

Fig. 4

Accelerated Aging in $\text{Ag}_{13}\text{I}_9\text{W}_2\text{O}_8$ Fast-Ion Optical Switches *

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ABSTRACT

Habbal et al.¹ discovered in 1978 an unusual photoelectric effect in the fast-ion conductor silver iodide tungstate, in which the presence of relatively low power densities of blue-green laser light results in an order-of-magnitude decrease in electrical conductivity (see Fig. 1). The mechanism hypothesized for this effect is the photo-production of electron-hole pairs, of which the electron rapidly neutralizes a silver ion. This process has an extraordinarily large quantum efficiency, because the neutral silver atom thus formed not only removes one charge carrier from the ionic conduction, but it also blocks the paths for other Ag^+ ions to move. The net effect is the reverse of that observed in all other solids demonstrating the photoelectric effect, since conductivity decreases, rather than increases, under illumination. The process is also highly reversible.

This process is extremely interesting from a device point-of-view, because it permits the development of an extremely fast, repetitive opening switch. Many fast, repetitive closing switches exist, utilizing photoconductive mechanisms, but the only fast opening switches known are essentially fuses, which are of course not repetitive. In the effort to develop this phenomenon into a practical device, we have performed detailed studies on $\text{Ag}_{13}\text{I}_9\text{W}_2\text{O}_8$. Unfortunately, we have discovered that the presence of laser light² greatly accelerates the known aging process in this compound. Silver, presumably driven by the photovoltaic effect, transports out on the surfaces. This plating effect is rapid and irreversible; we measure approximately 1 mm per hundred hours at 1 W/cm² of blue-green light. This effect may preclude commercialization of switches based on this material. However, the kinetics remain of academic interest.

1 F. Habbal, J. A. Zvirgzds, and J. F. Scott, J. Chem. Phys. 69, 4984 (1978);
J. F. Scott, F. Habbal, and J. A. Zvirgzds, J. Chem. Phys. 72, 2760 (1980).

2 S. A. Suthanthiraraj, Bull. Electrochemistry 2, 553 (1986).

* This work supported in part by SDIO funds administered through ONR.

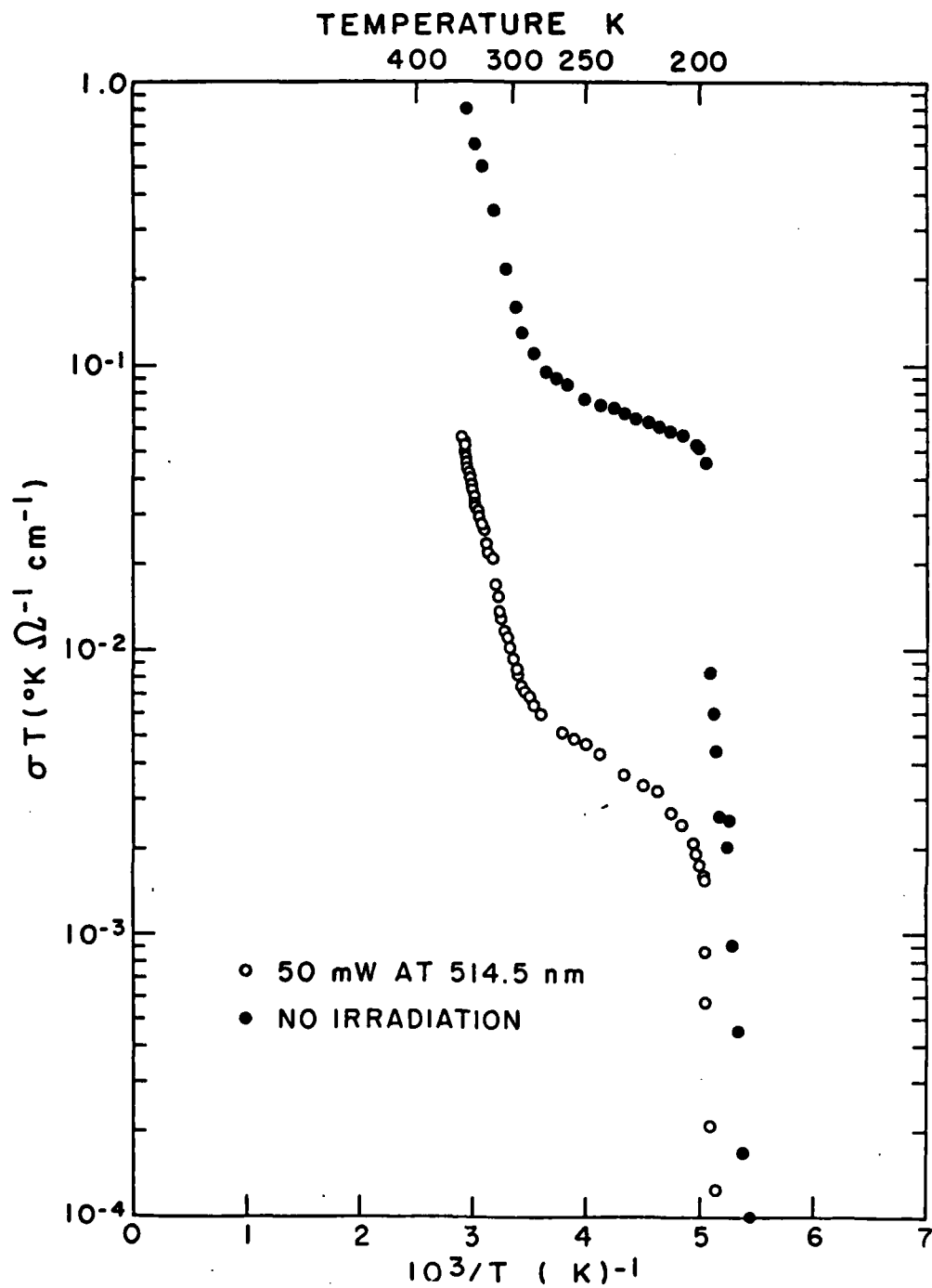


Figure 1: Electrical conductivity of $\text{Ag}_{26}\text{Te}_{18}\text{W}_4\text{O}_{16}$ as a function of temperature, with and without 1 W/cm^2 of 514.5 nm illumination.

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