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STUDY OF BOMBARDMENT-INDUCED-CONDUCTIVITY MATERIALS

N. H. Lehrer
Information Processing and Display Department

Interim Scientific Report No. 5
15 November 1961 through 14 January 1962

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ABSTRACT

The objective of this work is to conduct the necessary research to obtain the theoretical and experimental data concerning enhanced bombardment-induced-conductivity which will make possible the development of a direct-view storage tube with high resolution, selective erasure, and the simultaneous display of stored and nonstored information.

Primary effort was directed toward achieving further experimental confirmation of a correlation between increasing crystal size and higher values of the conduction ratio. It was established previously that thermal processing of the zinc sulfide increases the crystal size and that 300°C thermally processed films exhibited about twice the value of the conduction ratio of non-thermally processed films.

Measurements were made on films thermally processed at 450°C and 600°C. X-ray diffraction patterns indicated that these films exhibited progressively larger size crystals than 300°C processed layers.

Both the 450°C and the 600°C thermally processed layers were found to exhibit conduction ratio values lower than those of the 300°C thermally processed layers, but higher than those of the non-thermally processed layers.

This new evidence suggests that factors other than crystal size may play a significant role in the bombardment-induced-conductivity effect.
I. INTRODUCTION

Zinc sulfide layers thermally processed in hydrogen sulfide at 300°C had been found to exhibit about twice the conduction ratio of non-thermally processed films, as shown in Fig. 1. Also electron microscope and x-ray diffraction studies indicated that such thermally processed films exhibit a moderate growth in crystal size. These factors suggested the possibility of a correlation between increasing crystal size and higher values of the conduction ratio. Additional measurements of the conduction ratio as a function of the crystal size were required to confirm this correlation.

Because it had already been established that an additional moderate increase in crystal size could be achieved by processing the zinc sulfide layer at temperatures above 300°C, it appeared logical to measure the conduction ratio of such layers. Several obstacles were encountered in the fabrication of 600°C processed films, as indicated in the next section.

II. THERMAL PROCESSING OF THE ZINC SULFIDE LAYERS

A standard technique had been evolved for the preparation of zinc sulfide layers to be processed at 300°C. In this technique a soft glass microscope slide is used as the substrate material and aluminum as the electrode material. Processing of the layer could be accomplished successfully in either air or H₂S.

The 600°C schedule appeared to offer some additional problems:
1. Substrate: Processing at 600°C would require the use of hard glass instead of the soft glass.
2. Electrode Material: Aluminum melts at 660°C, and therefore it did not appear suitable for use.

The solution to these problems appeared straightforward:
1. Use hard glass substrate.
2. Utilize higher melting point materials for the electrodes.

Several zinc sulfide layers were prepared using hard glass substrates and chromium plated nickel as the electrode material. Processing of these films at 600°C in air, however, resulted in conversion of the zinc sulfide to zinc oxide.
Fig. 1. The conduction ratio versus primary-beam energy obtained with the low-energy holding-beam technique on thermally processed and unprocessed 0.5-micron zinc sulfide layers.
Processing of the layers in an H$_2$S atmosphere prevented conversion of the ZnS to ZnO. However, the chromium electrode material was rendered nonconductive by the H$_2$S. Other electrode materials were tried and found to be attacked by the H$_2$S. These materials included rhodium-plated nickel, chromium, nickel, platinum-palladium, and stannous oxide. (The stannous oxide remained a conductor where it was covered by the zinc sulfide.) Aluminum was found to be unaffected by the processing, although it had at first been thought that it would be rendered mechanically imperfect by heating close to its melting point.

The deposition of the zinc sulfide onto a heated substrate was also investigated to determine whether larger crystals could be obtained by this technique than by thermal processing. It was found that heating the substrate above 300°C prevented deposition of an appreciable layer of zinc sulfide onto the substrate. X-ray diffraction of layers deposited on heated substrates revealed that the crystal size was no greater than that which could be obtained by thermally processing the layers.

III. CONDUCTION RATIO MEASUREMENTS BY THE LOW-ENERGY HOLDING-BEAM TECHNIQUE ON THERMALLY PROCESSED FILMS

A. 450°C Thermally Processed Films

Several layers were prepared and thermally processed at 450°C. Fig. 2 indicates the conduction ratio as a function of the primary beam energy for three 450°C thermally processed films. Note that good agreement was obtained among all three samples.

In Fig. 3 the variation of the conduction ratio with voltage drop under bombardment with a 14 kv primary beam energy is shown. Here again good agreement is obtained among all three samples.

B. 600°C Thermally Processed Films

While many layers were processed at 600°C, most of them contained substantial amounts of hexagonal zinc sulfide. By increasing the heating and cooling time it was possible to produce a few films that were almost 100 percent cubic.

Fig. 4 indicates the conduction ratio as a function of primary beam energy for one 600°C thermally processed film; in Fig. 5 the variation of the conduction ratio with voltage drop across the layer is shown.
Fig. 2. The conduction ratio versus primary beam energy for 0.5-micron zinc sulfide layers thermally processed at 450°C in H₂S.
Fig. 3. The conduction ratio versus the voltage drop across the layer for 0.5-micron zinc sulfide layers thermally processed at 450°C in H₂S.
Fig. 4. The conduction ratio versus primary beam energy for a 0.5-micron zinc sulfide layer thermally processed at 600°C in H₂S.
Fig. 5. The conduction ratio versus the voltage drop across the layer for a 0.5-micron zinc sulfide layer thermally processed at 600°C in H₂S.
C. Discussion

A comparison of the data taken on the 450°C and 600°C processed layers with 300°C and non-thermally processed layers is shown in Figs. 6 and 7. In Fig. 6 the conduction ratio is given as a function of the primary beam energy. Note that although the 300°C processing has resulted in increased values of the conduction ratio, this was not the case for the 450°C and 600°C processing. It should be emphasized that the 450°C data are considered reliable since they have been duplicated on several samples, while the 600°C data have been obtained on only one layer.

In Fig. 7, the variation of the conduction ratio with voltage drop is indicated for the various thermal processing schedules. Here it is quite obvious that processing at 300°C resulted in substantial increase in conduction ratio in comparison with unprocessed layers as well as with those processed at still higher temperatures.

IV. CONCLUSIONS

1. Thermal processing of the zinc sulfide layers increases the value of the conduction ratio.

2. The increase in the conduction ratio with the temperature at which the processing is performed is not monotonic, but appears to peak at 300°C, based on existing data.

3. While some evidence exists that the conduction ratio increases with increasing crystal size, it is not always true that the larger the crystal size the greater the conduction ratio.

4. It appears that factors in addition to crystal size may play an important role in the BIC effect.
Fig. 6. The conduction ratio versus primary beam energy for layers receiving various thermal processing.
Fig. 7.
The conduction ratio versus the voltage drop across the layer for layers receiving various thermal processing.
V. RECOMMENDATIONS

To understand the nature of the bombardment-induced-conductivity effect, it is important to determine what factors other than crystal size are being changed as a result of the thermal processing. A study of the density of traps may provide a clue to determining these factors. Thus, by measuring and comparing the trap density in the various thermally processed layers it may be possible to correlate the variation in induced currents with the trap density. This can be understood by considering that under conditions of steady electron bombardment, the quantity of trapped charge constitutes a space charge which tends to retard the flow of current through the dielectric. It would therefore be expected that the higher values of the conduction ratio associated with particular thermal processing schedules will be found in materials with lower trap densities. Thus, part of the future effort should concern itself with investigation of the means for measuring the trap densities in the dielectric layers.

However, because this report covers the final period of the present Bombardment-Induced-Conductivity Materials Study Contract, the future effort should be largely determined by the requirements of the follow-on contract, "Demonstration of the Feasibility of a Meshless Storage Tube." For this follow-on contract the initial emphasis will be on construction and optimization of the equipment for measurement of the sustained bombardment-induced-conductivity effect. Consideration should be given to the measurement of trap densities on a low-priority basis.