

D. A. Lilly, D. E. Joslin, and H. K. A. Kan

The Aerospace Corporation  
El Segundo, California 90245

## ABSTRACT

The capacitance and conductance-voltage characteristics were measured on metal-insulator-semiconductor capacitors fabricated with zirconium dioxide films on single-crystal lead telluride. At 77 K, on both n- and p-type substrates, evidence of surface potential control was obtained. Comparison of the measured capacitance-voltage characteristics with those calculated from the equilibrium solution of the one-dimensional Poisson equation indicates qualitative agreement, although the slope ( $dC/dV$ ) of the measured capacitance in the region near the capacitance minimum is less steep than calculated. The high-frequency response of the capacitance and position of the capacitance minimum were used to deduce the presence of an inversion layer on some n-type substrates of charge density approximately  $5.0 \times 10^{13} \text{ cm}^{-2}$ . This layer was found to be dependent on surface preparation treatment prior to insulator deposition. Results of surface chemical studies indicate that inversion may be due to oxide formation during chemical etching. Conductance data obtained confirm the existence of a large interfacial state density.

## I. INTRODUCTION

The metal-insulator-semiconductor (MIS) structure was used in investigating the surface electronic properties of many semiconductors (Refs. 1-4). These properties are strongly determined by preparation and fabrication techniques and are revealed in measurements of the capacitance-voltage (C-V) and conductance-voltage (G-V) characteristics of MIS structures. In this paper the results of an investigation of the electronic properties at 77 K of MIS structures fabricated on monocrystalline lead telluride (PbTe) substrates are reported. Although several insulators and surface preparation techniques were investigated, the discussion here is limited to the results obtained for devices fabricated with zirconium dioxide ( $\text{ZrO}_2$ ) and prepared with two different chemical treatments.

## II. SAMPLE PREPARATION AND DEVICE FABRICATION

Wafers of p-type PbTe up to 1.5 mm thick were sliced and diced on a stainless steel wire saw (diamond impregnated blade of 0.010 in. diam) with a slurry of fine grit and glycerine. The crystal\* was characterized by small-angle grain boundaries; etching (Ref. 5) revealed etch pit densities of  $10^6 \text{ cm}^{-2}$  and, near grain boundaries, as great as  $10^8 \text{ cm}^{-2}$ . Room-temperature carrier concentration and mobility of the as-received crystal were  $2 \times 10^{18} \text{ holes cm}^{-3}$  (assuming  $p = (eR_H)^{-1}$ ) and  $735 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{sec}^{-1}$ , respectively. The normal to the sample surfaces was

determined to be within 5 deg of  $\langle 100 \rangle$ .

Sample carrier concentration was controlled by using an isothermal annealing technique that was described by Brebrick and Gubner (Ref. 6). Prior to annealing, the sample thickness was reduced to nominally 0.8 mm by lapping first on water-moistened 600 grit paper and then on a silk-covered wheel with 0.3  $\mu\text{m}$  alumina powder moistened with a detergent-water solution. A final 1 to 5  $\mu\text{m}$  of material was removed by lapping on a felt wheel with a solution of iodine and methanol (Ref. 7). Samples were then rinsed thoroughly in methanol and distilled water and sealed off in an annealing ampoule at a pressure of less than  $10^{-6}$  Torr.

Following annealing and immediately prior to insulator deposition, one of two final surface treatments was used. In order to remove approximately 1  $\mu\text{m}$  of material, all samples were again lapped on a felt wheel with a solution of iodine and methanol, rinsed in methanol and distilled water, and dried in a stream of argon gas. An additional 2  $\mu\text{m}$  of material were removed from some of these samples during a second treatment that consisted of the following process (Ref. 8):

1. Immerse for 10 s in a 9/1 solution of potassium dichromate and nitric acid
2. Rinse in distilled water
3. Immerse for 30 s in a solution of warm ( $40^\circ \text{C}$ ) 50% sodium hydroxide
4. Rinse in distilled water
5. Immerse in dilute HCl
6. Rinse in distilled water
7. Dry in a stream of argon gas.

Samples were immediately mounted in special holders for deposition of  $\text{ZrO}_2$  in an oil-pumped, electron-beam evaporator system. Spectrographic grade  $\text{ZrO}_2$  (pressed powder from Wah Chang Corporation or grey pellets from EM Laboratories, Inc.) was outgassed at a moderate temperature (a few hundred degrees centigrade) before being deposited in a controlled oxygen background pressure of  $5 \times 10^{-4}$  Torr at a rate of 20-25  $\text{\AA}/\text{s}$ . No effort was made to control the substrate temperature, which may have increased to approximately  $40^\circ \text{C}$  during the deposition. Deposition times were limited in order to obtain film thickness of approximately 1500  $\text{\AA}$ .

Circular field electrodes (30  $\text{\AA}$  chromium, 500  $\text{\AA}$  gold, and 2  $\mu\text{m}$  indium) were evaporated through a hard mask with apertures of  $4.2 \times 10^{-4}$  and  $1.4 \times 10^{-4} \text{ cm}^2$  by standard electron beam procedures. This step required a brief exposure

\* Purchased from Atomergic Chemical Company, Long Island, New York.

of the substrates to the ambient for placement of samples in the mask holders.

### III. C-V AND G-V RESULTS

For a basis of comparison with experimental results, calculated C-V characteristic curves are presented in Fig. 1 for the low- and high-frequency response of a PbTe MIS capacitor following the full statistical treatment of Marcus (Ref. 9). Results are shown for n-type substrates with temperature = 77 K, carrier concentration =  $5 \times 10^{17} \text{ cm}^{-3}$ , ratio of insulator dielectric constant to thickness =  $10^{-2} \text{ \AA}^{-1}$ . PbTe band and material parameters were taken from a review article by Dalven (Ref. 10). It is clear from Fig. 1 that small capacitance changes are to be expected experimentally, and that insulator dielectric strengths in excess of  $10^6 \text{ V-cm}^{-1}$  are required in order to obtain surface potential control.

C-V characteristic curves obtained at 77 K for MIS structures fabricated on n- and p-type substrates are shown in Fig. 2. On most devices, insulator breakdown voltages were greater than  $5 \times 10^6 \text{ V-cm}^{-1}$ ; the film dielectric constant was determined to be approximately 15. These C-V characteristics are typical of those obtained on devices that received the iodine-methanol surface treatment prior to insulator deposition. The capacitance minima appear at a positive (negative) voltage for p-type (n-type) substrates, as expected. The small changes in capacitance, of the order of 3%, are consistent with calculations, but the slope ( $dC/dV$ ) of the measured capacitance in the region near the capacitance minimum is less steep than calculated. It should be noted that these curves were obtained after the structures were baked for 65 h in air at  $80^\circ\text{C}$ , which dramatically reduced hysteresis effects in the iodine-methanol polished samples.

The C-V characteristic curves obtained for the n-type device shown in Fig. 2 at 1, 10, and 100 kHz are shown in Fig. 3. The variation in capacitance at different frequencies can be attributed to the frequency dependence of the  $\text{ZrO}_2$  capacitance that was observed in measurements of metal-insulator-metal (MIM) capacitors fabricated with the MIS capacitors. The closed points were obtained by subtracting a small voltage-dependent MIM capacitance (Fig. 4) from the total measured MIS capacitance. The primary effect of such a calculation is to flatten the characteristic at large applied bias such that the attainment of the accumulation capacitance at  $V_b \approx 20 \text{ V}$  is implied.

In Fig. 3, the transition to high-frequency behavior occurs near 100 kHz. This frequency is much greater than the high-frequency limit (approximately 100 Hz for a minority carrier lifetime of 5 ns) calculated from bulk considerations (Ref. 11). It is concluded, therefore, that interfacial states determine the frequency response of the device up to approximately 100 kHz. The contribution of these interfacial states to the capacitance depends on frequency and bias, as can be seen in the region of negative bias for curves A and B (Fig. 3). This interfacial behavior is reflected by the G-V characteristics that were obtained on this device (Fig. 5). Such overall behavior indicates the presence of an equivalent

interfacial state capacitance comparable in magnitude to the depletion layer capacitance ( $\approx 8 \times 10^{-7} \text{ F/cm}^2$ ).

The C-V characteristic curves in Fig. 6 were obtained for an MIS structure whose surface was treated with the potassium dichromate-nitric acid solution as described in Section II. These curves are typical of those obtained with this surface treatment and show large hysteresis effects. Neither a bake for 24 h in air at  $80^\circ\text{C}$  nor bakes for 1 h in flowing hydrogen gas at  $80^\circ\text{C}$  and 3 h at  $150^\circ\text{C}$  reduced the hysteresis or altered the C-V and G-V characteristics. Evidently, this highly oxidizing treatment results in the creation of an interfacial trap level (or levels) that is stable with respect either to further oxidation (air-bake) or reduction (hydrogen bake). Furthermore, the position of the capacitance minimum at positive gate bias in Fig. 6 indicates that the surface of the n-type substrate is inverted and becomes somewhat less inverted with increasing frequency. For inversion to occur, a negative charge layer of magnitude approximately  $1/q (C\Delta V) \approx 9.0 \times 10^{13} \text{ e}^-/\text{cm}^2$  is required. The presence of this layer may also be the result of the surface treatment.

On several devices prepared with the second treatment, however, the capacitance minimum moved across the  $V_B = 0$  axis for sufficiently large voltage excursions (Fig. 7). Such effects have been reported on MIS structures of anodic oxides on p- and n-type indium antimonide (2) and may be due to interfacial traps for majority as well as minority carriers. Since this capacitance minimum shift did not occur over a  $\pm 80 \text{ V}$  range of similarly prepared p-PbTe, however, it appears that interfacial traps for majority carriers only are sufficient qualitatively to explain such behavior.

In an effort to relate the chemical composition of the surface to the measured electrical properties, x-ray photoelectron spectra were obtained on samples that had received the surface treatments described. Preliminary spectra show a pronounced difference between the peak height ratios of two tellurium peaks (the  $3d_{5/2}$  and  $3d_{3/2}$ ) to their associated oxides. Identification of the peaks was aided by an independent run with pure tellurium and comparison with previously reported lead telluride and tellurium oxide spectra (Ref. 12). It is not now known, however, whether the tellurium peaks should be associated with neutral tellurium or a charged state. Nevertheless, these preliminary results indicate that the effect of the second surface treatment with potassium dichromate and nitric acid relative to the first with iodine and methanol is to increase the surface tellurium concentration relative to the tellurium-oxide concentration. We believe, therefore, that the electrical activity of the PbTe- $\text{ZrO}_2$  interface increases as the surface concentration of tellurium (perhaps  $\text{Te}^{2-}$ ) increases relative to the concentration of  $\text{TeO}_2$ .

### IV. CONCLUSIONS

These experimental results are important for assessing the suitability of PbTe for use as substrate material in charge-coupled devices. The results indicate that two initial requirements for such use have been met in (1) obtaining an

electrically stable insulator of high dielectric strength, and (2) demonstrating surface potential control from accumulation through inversion in a manner generally consistent with theoretical expectations. Such consistency, it should be noted, was not shown by previously reported C-V data obtained on PbTe films (Ref. 13). The most successful results have been obtained on substrates that were prepared with an iodine-methanol polish.

Interfacial state densities remain high, however, and must be reduced if efficient charge transfer or charge injection is to be realized. More work is required, particularly in surface preparation, in order to passivate the surface and develop the relationships between surface preparation and surface electrical properties.

#### REFERENCES

1. Nicollian, E. H., and Goetzberger, A., "The Si-SiO<sub>2</sub> Interface-Electrical Properties as Determined by the Metal-Insulator-Silicon Conductance Technique," *Bell Syst. Tech. J.*, Vol. 46, No. 6, p. 1055, July-August 1967.
2. Kim, J. C., "InSb MOS Detector," Final Technical Report, Army Night Vision Laboratory, Contract No. DAAK02-73-C-006, General Electric Company, Syracuse, New York, February 1975.
3. Leonberger, F. J., McWhorter, A. L., and Harman, T. C., "PbS MIS Devices for Charge-Coupled Infrared Imaging Applications," *Appl. Phys. Lett.*, Vol. 26, No. 12, p. 704, June 1975.
4. Schwartz, R. J., Dockerty, R. C., and Thompson, H. W., Jr., "Capacitance Voltage Measurements on n-Type InAs MOS Diodes," *Solid State Electron.*, Vol. 14, No. 2, p. 115, February 1971.
5. Houston, B. B., and Norr, M. K., "Dislocation Etch Pits on p-Type Lead Telluride," *J. Appl. Phys.*, Vol. 31, p. 615, 1960.
6. Brebrick, R. F., and Gubner, E., "Composition Stability Limits of PbTe. II," *J. Chem. Phys.*, Vol. 36, No. 5, p. 1283, March 1962.
7. Calawa, A. R., Harman, T. C., Finn, M., and Youtz, P., "Crystal Growth, Annealing, and Diffusion of Lead-Tin Chalcogenides," *Trans. Metall. Soc. AIME*, Vol. 242, No. 3, p. 374, March 1968.
8. Lorenz, M. R., "A Chemical Polish for Lead Telluride," *Electrochem. Soc.*, Vol. 112, No. 2, p. 240, February 1965.
9. Marcus, Paul M., "Calculation of the Capacitance of a Semiconduction Surface with Application to Silicon," *IBM J. Res. Dev.*, Vol. 8, No. 5, p. 496, November 1964.
10. Dalven, R., "A Review of the Semiconductor Properties of PbTe, PbSe, PbS, and PbO," *Infrared Phys.* Vol. 9, No. 4, p. 141, December 1969.
11. Hofstein, S. R., and Warfield, G., "Physical Limitations on the Frequency Response of a Semiconductor Surface Inversion Layer," *Solid State Electron.*, Vol. 8, No. 3, p. 321, March 1965.
12. Grant, R. W., Paska, J. G., Long, J. T., and Andrews, A. M., "ESCA Surface Studies of Pb<sub>1-x</sub>Sn<sub>x</sub>Te Devices," *J. Vac. Sci. Technol.*, Vol. 13, No. 4, p. 940, July-August 1976.
13. Tao, T. F., Ellis, J. R., Kost, L., and Doshier, A., "Feasibility Study of PbTe and Pb<sub>0.76</sub>Sn<sub>0.24</sub>Te Infrared Charge-Coupled Imager," Proceedings of the CCD Applications Conference, pp. 249-268, Naval Electronics Center, San Diego, September 1973.

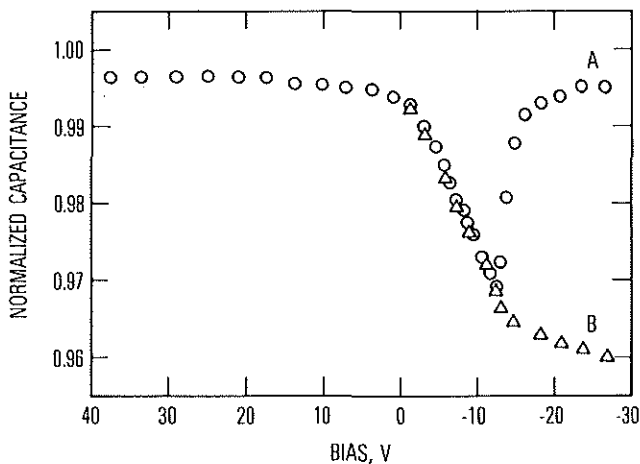


Fig. 1. Calculated low-frequency (A) and high-frequency (B) C-V characteristics for a PbTe MIS capacitor.

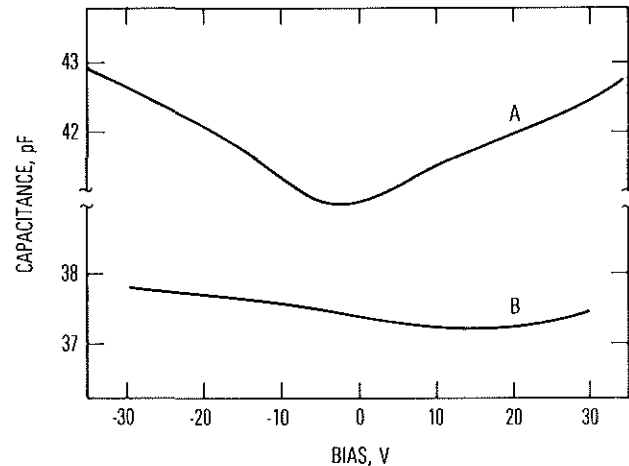


Fig. 2. Experimental C-V characteristics for an iodine-methanol treated PbTe MIS device. Curve A,  $n = 2.0 \times 10^{17}/\text{cm}^3$ ; curve B,  $p = 1.4 \times 10^{18}/\text{cm}^3$ .

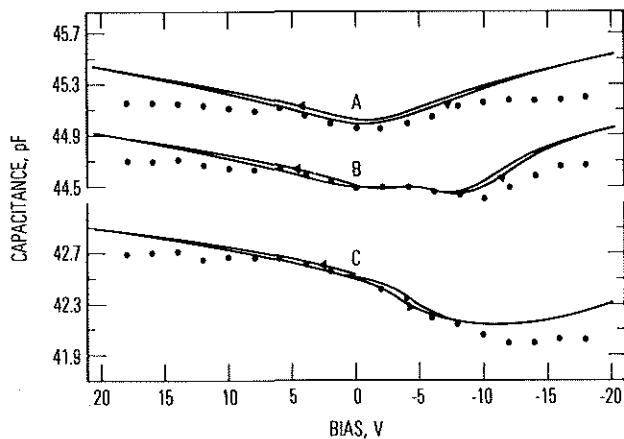


Fig. 3. Experimental C-V characteristics for the iodine-methanol treated PbTe MIS device in curve A of Fig. 2. Field plate area =  $4.9 \times 10^{-4} \text{ cm}^2$ , insulator thickness =  $1590 \text{ \AA}$ , voltage sweep rate =  $40 \text{ V/min}$ . Curve A,  $f = 10^3 \text{ Hz}$ ; curve B,  $f = 10^4 \text{ Hz}$ ; curve C,  $f = 10^5 \text{ Hz}$ .

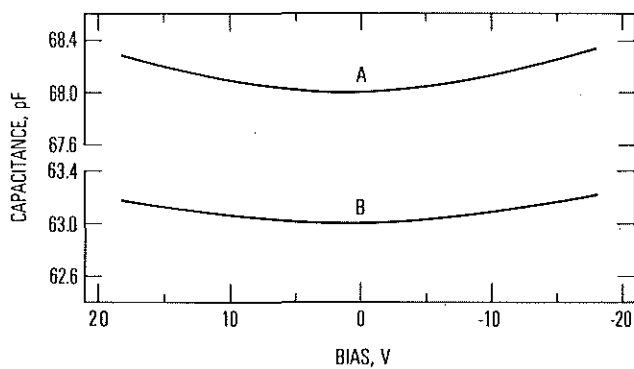


Fig. 4. Experimental C-V characteristics for a  $\text{ZrO}_2$  MIM device. Curve A,  $f = 10^3 \text{ Hz}$ ; curve B,  $f = 10^5 \text{ Hz}$ .

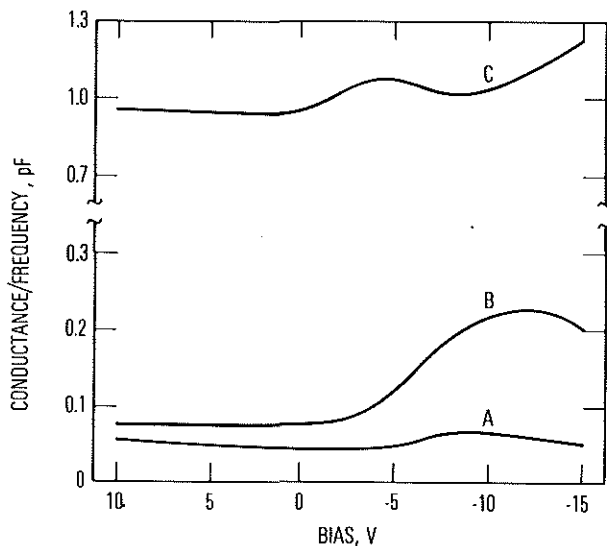


Fig. 5. Experimental G-V curves for the iodine-methanol treated device in Fig. 3. Curve A,  $f = 10^3 \text{ Hz}$ ; curve B,  $f = 10^4 \text{ Hz}$ ; curve C,  $f = 10^5 \text{ Hz}$ . Voltage sweep rate =  $40 \text{ V/min}$ .

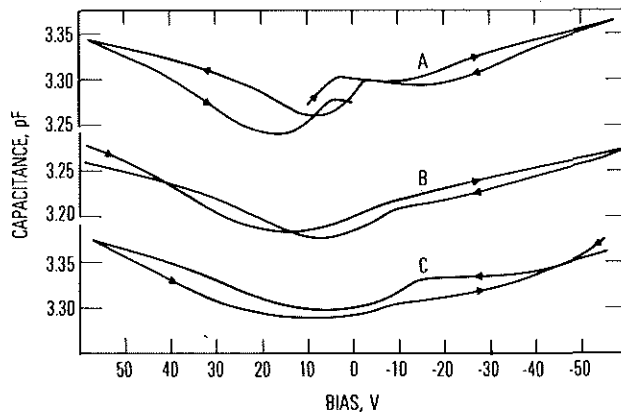


Fig. 6. Experimental C-V curves for a potassium dichromate-nitric acid treated PbTe MIS device. Carrier concentration =  $5 \times 10^{17} / \text{cm}^3$  (n-type); insulator thickness =  $1500 \text{ \AA}$ ; field plate area =  $4.5 \times 10^{-5} \text{ cm}^2$ . Curve A,  $f = 10^3 \text{ Hz}$ ; curve B,  $f = 10^4 \text{ Hz}$ ; curve C,  $f = 3 \times 10^4 \text{ Hz}$ .

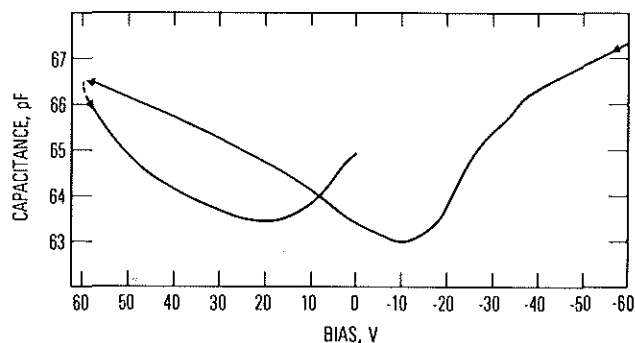


Fig. 7. Experimental C-V characteristics for a potassium dichromate-nitric acid treated n-type PbTe substrate.  $f = 10^3 \text{ Hz}$ .