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STRUCTURE, PROPERTIES AND RADIATION SENSITIVITY OF ELECTRICALLY BISTABLE MATERIALS

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Submitted by

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STRUCTURE, PROPERTIES AND RADIATION SENSITIVITY OF ELECTRICALLY BISTABLE MATERIALS

Abstract

This report describes work carried out during the first six-month period on a project directed towards a thorough electrical and metallurgical characterization of selected amorphous semiconducting materials.

Equipment for bulk glass preparation has been set up and some thin film structures have been fabricated by flash evaporation techniques. Work has commenced on local order structural measurements and electrical characterization of binary germanium tellurium alloys. It is intended that this study will be extended into more complicated systems as the project continues.

Work has commenced on systems based on the vanadium, phosphorus and potassium oxides, and a new crystalline phase has been discovered within this system. A comparative study of the electronic properties of crystalline materials and glasses having the same composition is being carried out. Finally, degradation of thin film electrodes has been observed under certain conditions and is being investigated.

INTRODUCTION

This report describes work carried out during the six months period of February to July, 1970. The project is directed towards a thorough electrical and metallurgical characterization of selected amorphous semiconducting materials of interest for use in the fabrication of electrical switching devices (ovonic devices). From a continuing assessment of current literature, it is becoming increasingly clear that the memory switching effect is based on a material structural transition giving rise to the formation of a high conductivity path between the electrodes, thus device parameters such as switching threshold voltage and its temperature dependence, delay time, and operating stability are very considerably determined by metallurgical processes occurring within the device.

This first six-month period has been one of project initiation and of technique development for the preparation and evaluation of chalcogenide and oxide electronic glasses. Equipment for encapsulation and glass fabrication has been established, and thin film structures have been prepared by flash evaporation. Work has commenced on both local order structural measurements and on electrical characterization. An ion milling machine has been obtained for thinning glasses for observation by electron microscopy. Finally, electrode degradation effects have been observed and are receiving particular attention.

PROJECT REPORT

1. Glass Preparation

i) Chalcogenides. Materials of 99.999% (or near) purity were weighed and placed in quartz ampoules. The ampoules were evacuated to approximately 10^{-5} torr and backfilled to about 10 cm of mercury with purified argon. The ampoules were sealed and placed in a furnace for a number of hours at 1000°C with occasional shaking. The ampoules were then allowed to cool in air or were forcibly cooled by an air blast.

ii) Vanadium oxide glasses. Bulk samples of P_2O_5-V_2O_5, P_2O_5-$2V_2O_5$ and K_2O-P_2O_5·$2V_2O_5$ were prepared in both crystalline and glassy forms using conventional techniques. Mixtures of high purity oxides were melted in covered platinum crucibles at 200°C above the melting point of the mix. Glass specimens were then cast in stainless steel moulds and annealed in air at 200°C.

iii) Thin films. A simple vibrating feed has been set up to allow particles of the starting material to fall into a crucible held at high temperature. Films were deposited from both pulverized glass of the required composition, and from elemental constituents ground together. From current literature, it is known that switching devices may be fabricated in either manner, but no information is available at this stage concerning the relationship between fabrication conditions and film properties of microstructure. Films have been deposited having thickness from a few 1000 Å to a few μ having

compositions TeGe, TeGe (80/20), TeSi (80/20) and TeAsSeGe (48:30:12:10). The vacuum system base pressure varied from about 5×10^{-5} torr, without cold trap charged, to about 5×10^{-7} torr with cold trap in operation.

2. Composition Analysis

Standards have been prepared for composition determination in the Te, As, Si and TeAsGe systems. Initially, erratic results were found to be due to the region of glass beneath the beam being actually molten during observation. This was subsequently avoided by considerably defocussing the electron probe.

3. Microstructure

An ion beam machine has been obtained and is to be used for thinning glass specimens for observation by transmission electron microscopy. The preparation of microscopy specimens from bulk glasses has been a notoriously difficult problem and should be greatly facilitated by the ion milling device. Observations on thin films are simpler, requiring only the stripping of the film from the substrate. Electron microscopy is expected to be a major feature in future phases of this work.

4. Atomic Order

Difficulty has been experienced in obtaining polished samples of glass suitable for measurement in the x-ray diffractometer due to the tendency for the specimen to fracture on removal from the quartz ampoule. Meanwhile, experience has

been gained with several arrangements designed to eliminate experimentally the Compton background present at high angles in the x-ray pattern. This is of major importance for obtaining a reliable radial distribution function.

Electron diffraction observations are in progress to attempt to compare the structure of flash evaporated mixed elements and flash evaporated crushed glasses. At a later date it is hoped that direct comparison may be made with x-ray observation of the local order in the glass prior to evaporation.

Measurements on GeTe (50:50) have been carried out repeating previous electron diffraction[1] work, and x-ray work by Bienenstock et al.[2] The intensity curve obtained with the scanning electron diffraction system with electrostatic elimination of the inelastically scattered electrons is shown in Fig. 1. The radial distribution curve of Fig. 2 was obtained by taking the Fourier transform of $S[I(s)/N(f_1^2+f_2^2) - 1]$, where f_1, f_2 are the atomic scattering factors for Ge, Te respectively. As found previously, the nearest neighbor distance is ~2.6 Å, approximately the sum of the Ge and Te atomic radii. The nearest neighbor coordinate is approximately 3-fold

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[1]D. B. Dove, M. B. Heritage, K. L. Chopra and S. K. Bahl, Appl. Phys. Letters, 16, 138 (1970).

[2]A. Bienenstock, F. Betts and S. Ovshinsky, J. Non-Crystalline Solids, to appear (International Conference Proceedings).

in agreement with Bienenstock et al., but somewhat smaller than found previously by electron diffraction. It is quite clear that the local order is unlike that of crystalline GeTe. These measurements are being extended to a range of binary compositions and to more complicated systems.

5. Electrical Measurements

i) Bulk. Previous studies in this laboratory established the importance of thermal history in determining the electronic behavior of amorphous semiconductors. However, a detailed interpretation of the thermal treatment effects was not possible due to the lack of electronic data on multicomponent glasses and crystals of the same composition. For this reason, glasses and crystals of equivalent composition in the K_2O-P_2O_5-V_2O_5 system were investigated during this six-month period. The compositions studied were: P_2O_5-V_2O_5, P_2O_5-$2V_2O_5$, and K_2O-P_2O_5-$2V_2O_5$. Glass compositions will be denoted as P-V, P-V_2, and K-P-V_2 and the crystal phases will be designated PV, PV_2, and KPV_2.

The PV_2 crystal phase was first established as a separate phase in this study. X-ray diffraction, melting point, crystallization point, and optical phase analysis were used as tools to identify the new phase. Properties of the PV_2 crystals proved especially interesting. A very high room temperature D.C. conductivity of 10^{-2} $ohm^{-1}cm^{-1}$ was measured for the crystals in contrast to a value of 10^{-4} $ohm^{-1}cm^{-1}$ for the P-V_2 glasses. In contrast to this behavior, PV crystals are

lower in D.C. conductivity, at 25°C, than P-V glasses and KPV_2 crystals have nearly the same conductivity as K-P-V_2 glasses. The activation energy for D.C. and A.C. conduction, the mechanism of dielectric losses, and the frequency dependence of the conduction and capacitance of the crystal and glass states of all three compositions were measured and interpreted in terms of polaron theory and heterogeneous dielectrics.

The results of this investigation established that large thermal dependent changes in the electronic behavior of amorphous semiconductors can be attributed to the development of high conductivity microheterogeneities in the material. If crystalline heterogeneities of conductivity equivalent to that of the matrix are present in the material, the results show that the material is independent of thermal history. (Full details will be presented in later reports.)

ii) Thin films. Thin films of compositions GeTe (50/50), TeS (80/20), and TeAsSiGe (48/30/12/10) have been flash evaporated using starting materials of electronic grade purity. The films were deposited onto glass slides carrying thin film metallic electrodes. Upper electrodes were then deposited, yielding a group of about 40 planar capacitors of lateral dimensions 0.084 by 0.23 cm. Aluminum electrodes have been used for initial measurements; a sputtering system is being set up for depositing molybdenum or tantalum electrodes for switching investigations.

Measurements have been made of conductance and capacitance at room temperature over the frequency range 0 to 1 Mhertz,

using very small applied veltages. Frem these measuremonts the cenductivity, dielectric censtant and loss tangent as a functien ef frequency were determined as shewn in Figs. 3-6. Some results for TeSi (80/20) films are shown in Fig. 7.

By increasing the applied voltage the non-linear characteristic of Fig. 8 was obtained; however, it was noted that driving inte the nen-linear regien led in all cases to rapid deterieration of the Al electrodes, and a change in the current veltage curve. To show that it is net an essentially thermal effect, very shert (few μ sec) high veltage pulses were applied at a very low repetition rate (few/sec) and a similar deterioratien ceuld be observed. After predueing electrode deterioratien the capacitance/frequency curves were repeated and were feund to have changed in value very considerably.

Optical microscope and scanning electren micrescepe ebservations of a typical upper electrode, shown in Fig. 9a, indicate the presence ef blisters and other marks. These grew in size and frequently coalesced as the applied veltage was increased within the nen-linear region. After insertien into a vacuum system the blisters were found te have cellapsed as shown in Fig. 9b. Some films were subjected to an applied voltage inside an ultrahigh vacuum system equipped with a quadrapole mass analyzer; se far no change in gas background ceuld be detected as the veltage was applied. This experiment is to be repeated te attempt te establish whether the blistering is due to an electrede/glass reactien leading to less of adhesion, or whether there is actual gas evolution.

Summary

During this first six-month period, work has been initiated on the preparation and characterization of amorphous semiconductors both in bulk and thin film form. A start has been made on electrical characterization of selected bulk and thin film materials. A new phase has been found in the vanadium oxide glass system and the electrical characteristics of crystalline and glassy phases of the same composition have been made. Finally, some electrode degradation effects have been observed and are being studied in view of the potential importance of glass/electrode reactions on device stability.

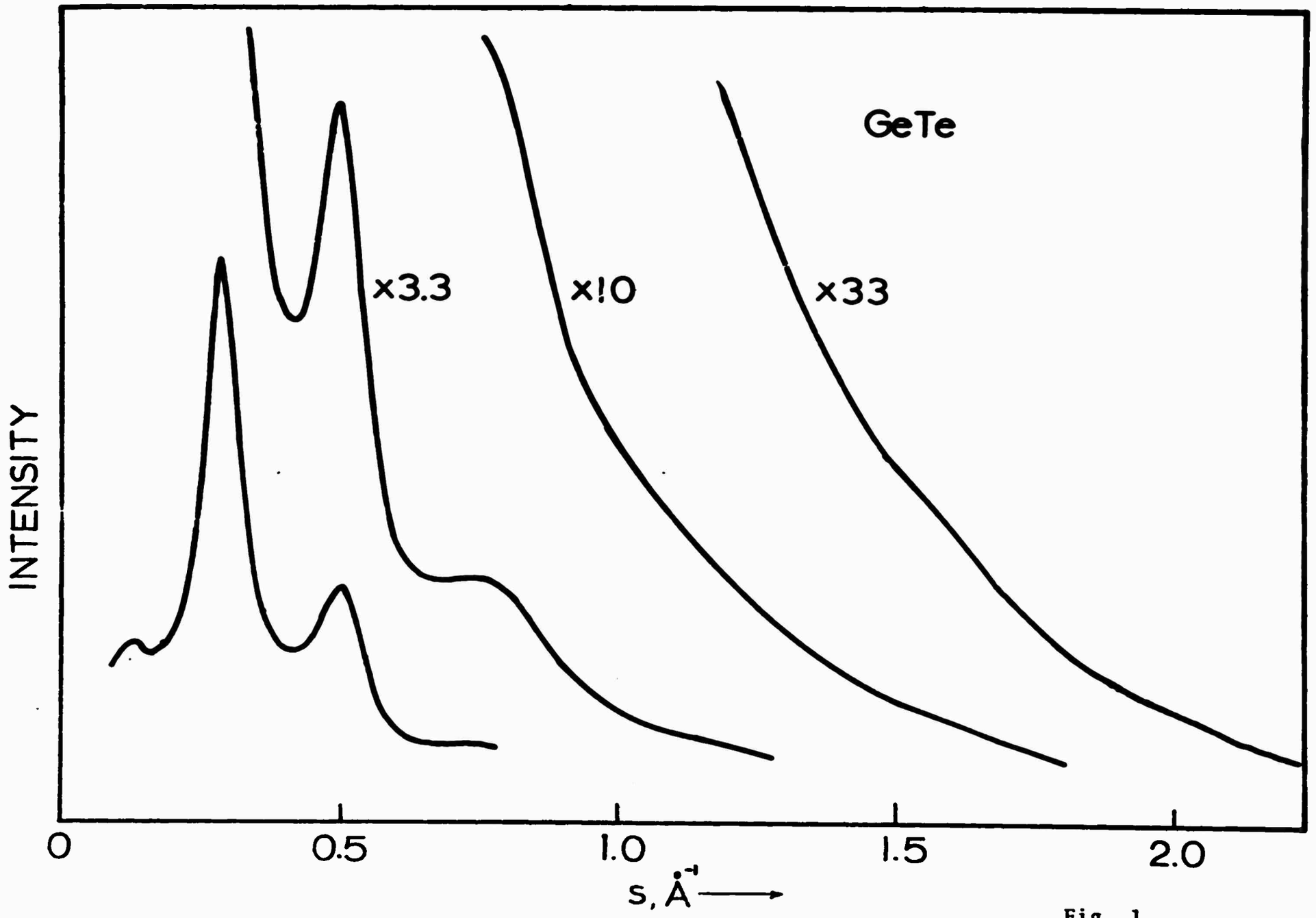

Fig. 1

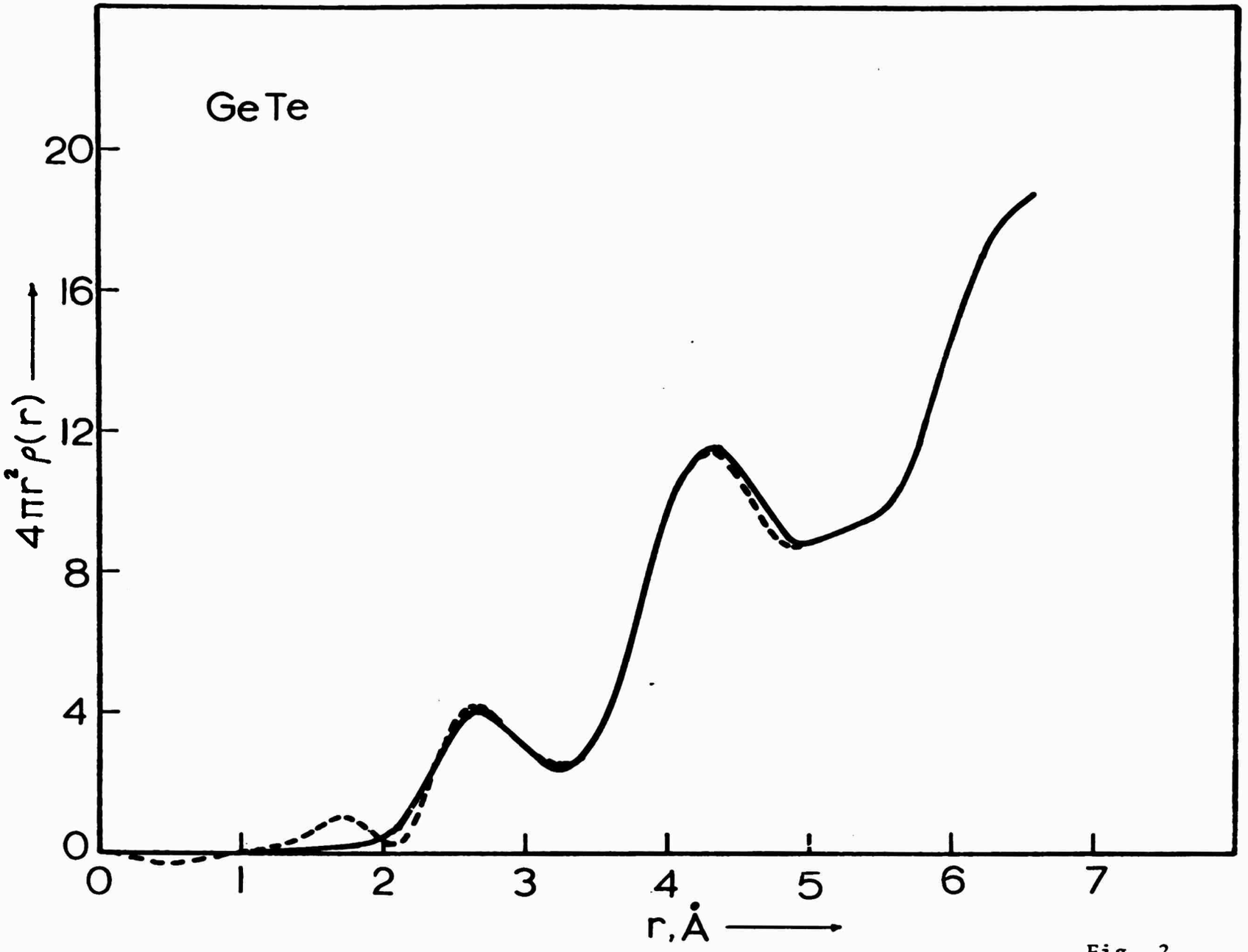

Fig. 2

Conductivity vs. Frequency for a
Thin Film GeTe Capacitor

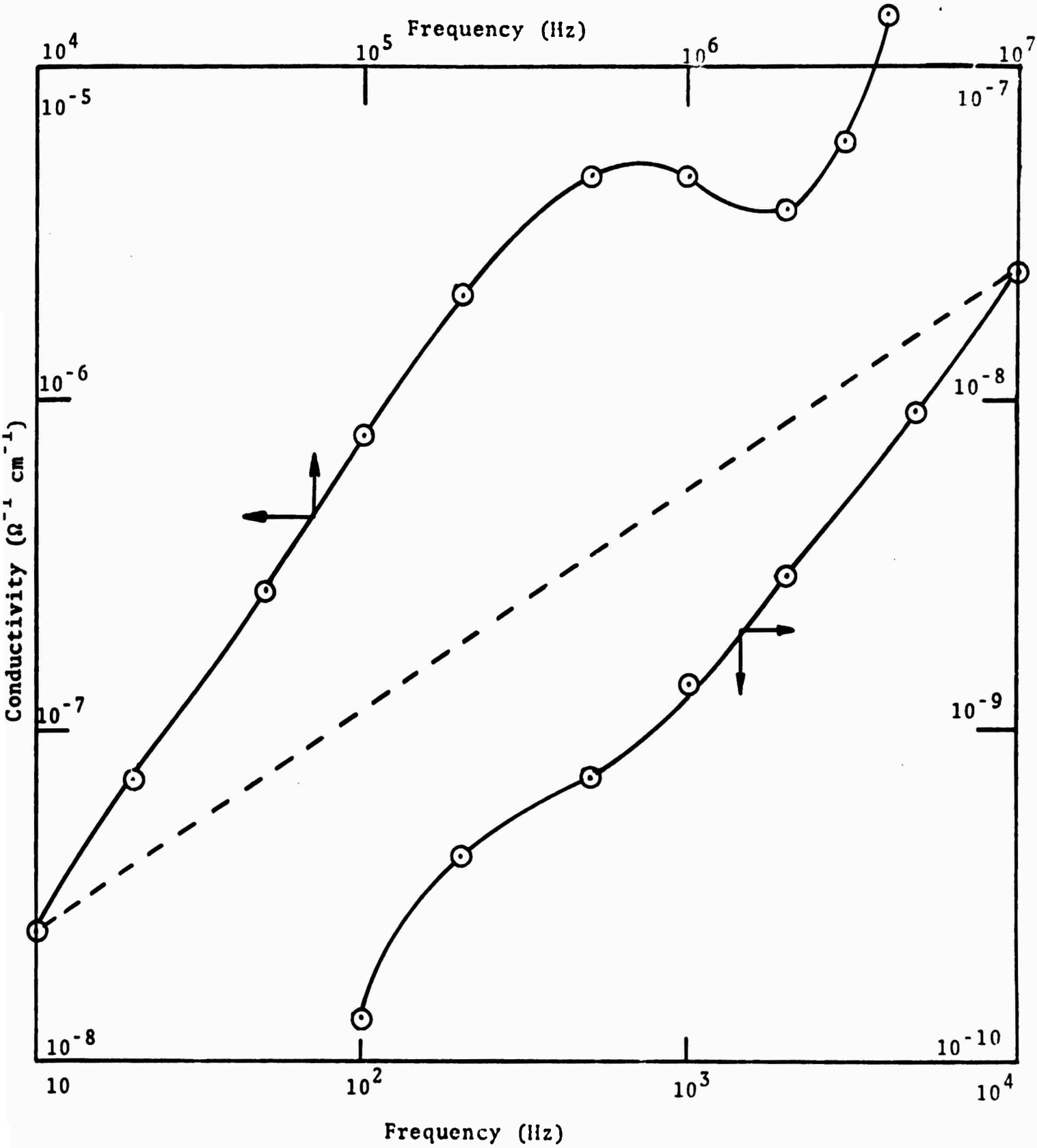

Fig. 3

Capacitance vs. Frequency for a
Thin Film GeTe Capacitor

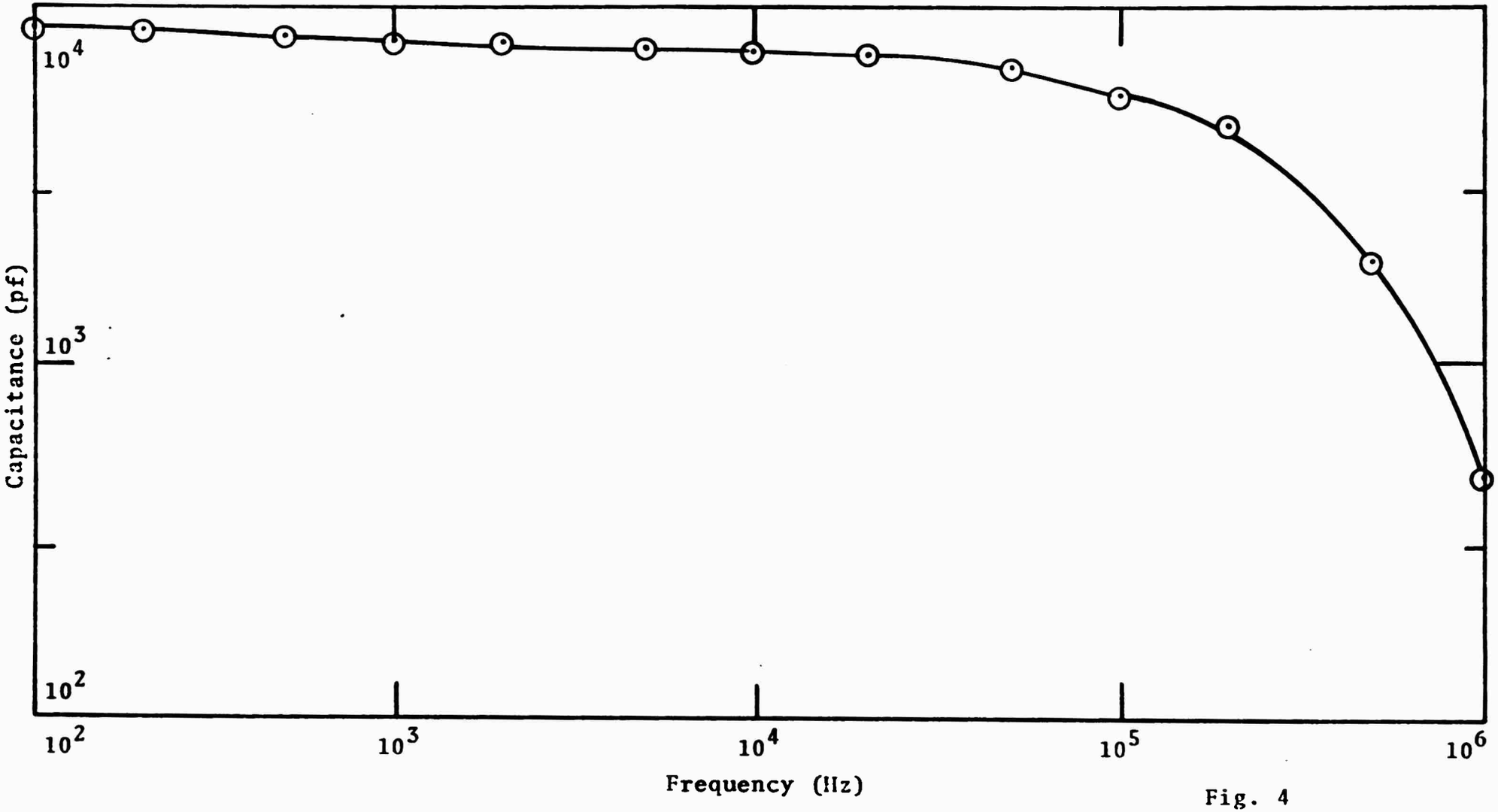

Fig. 4

Loss Tangent vs. Frequency for a
Thin Film GeTe Capacitor

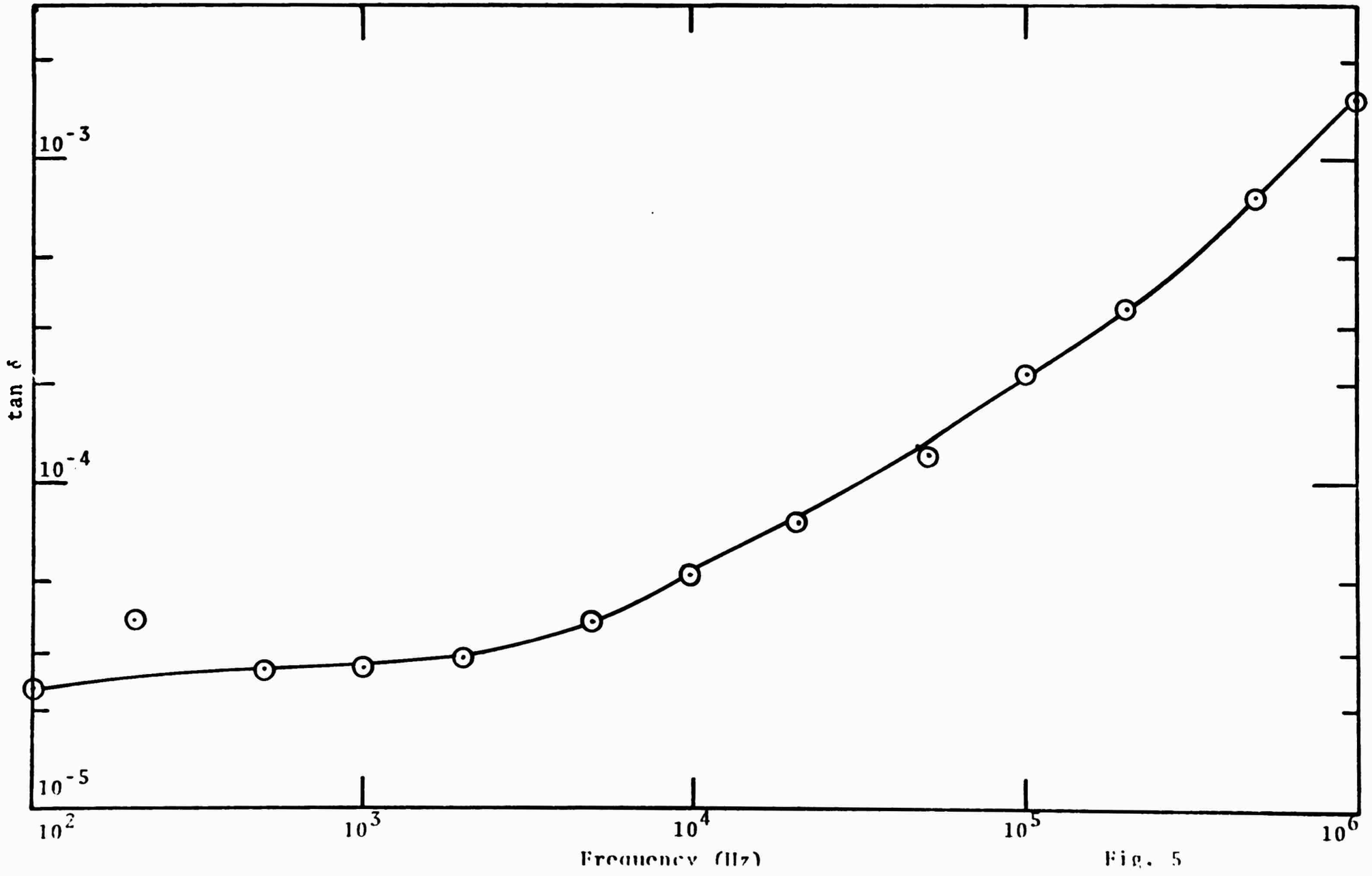

Fig. 5

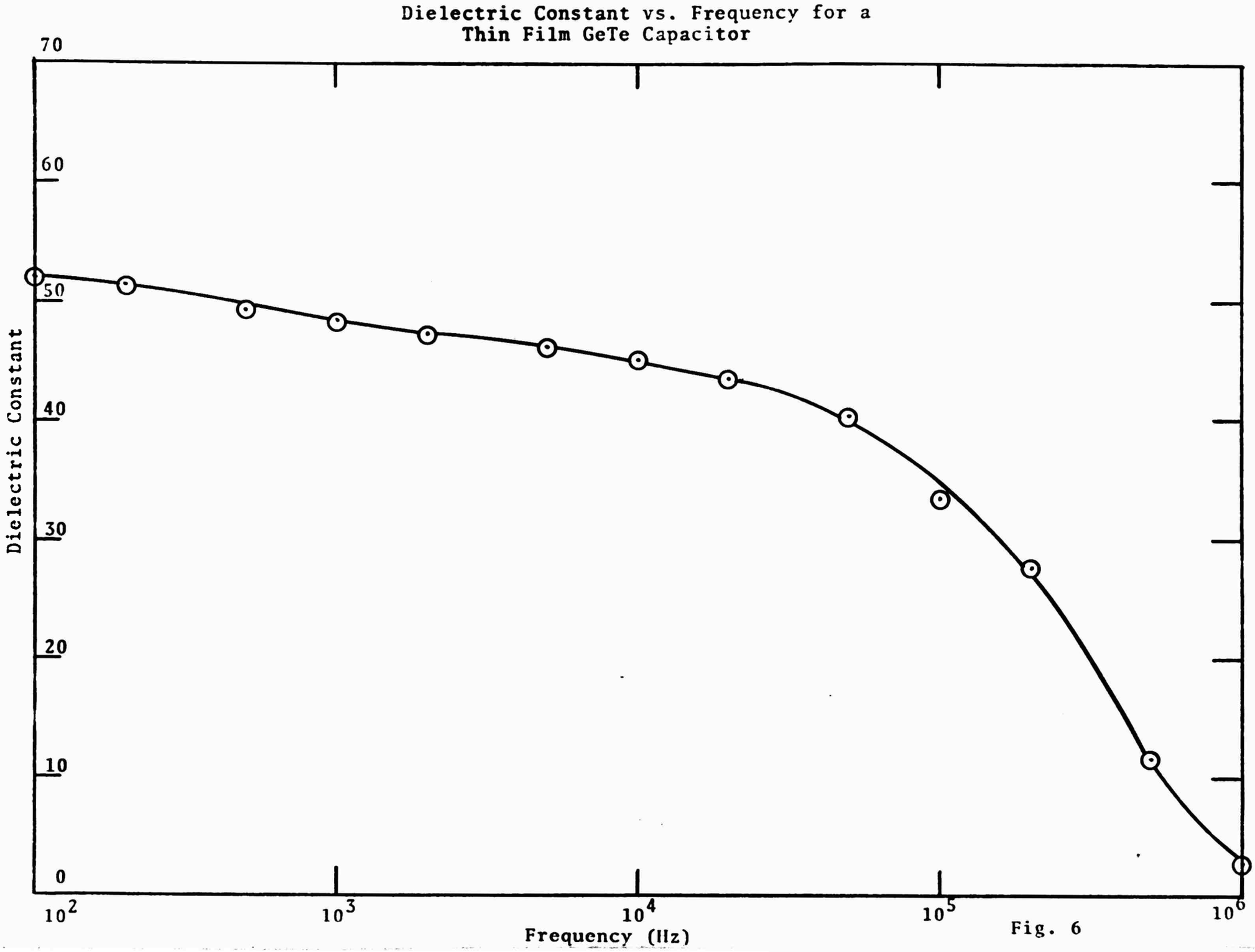
Dielectric Constant vs. Frequency for a
Thin Film GeTe Capacitor
70
60
50
40
30
20
10
0
Dielectric Constant
10^2
10^3
10^4
10^5
10^6
Frequency (Hz)

Fig. 6

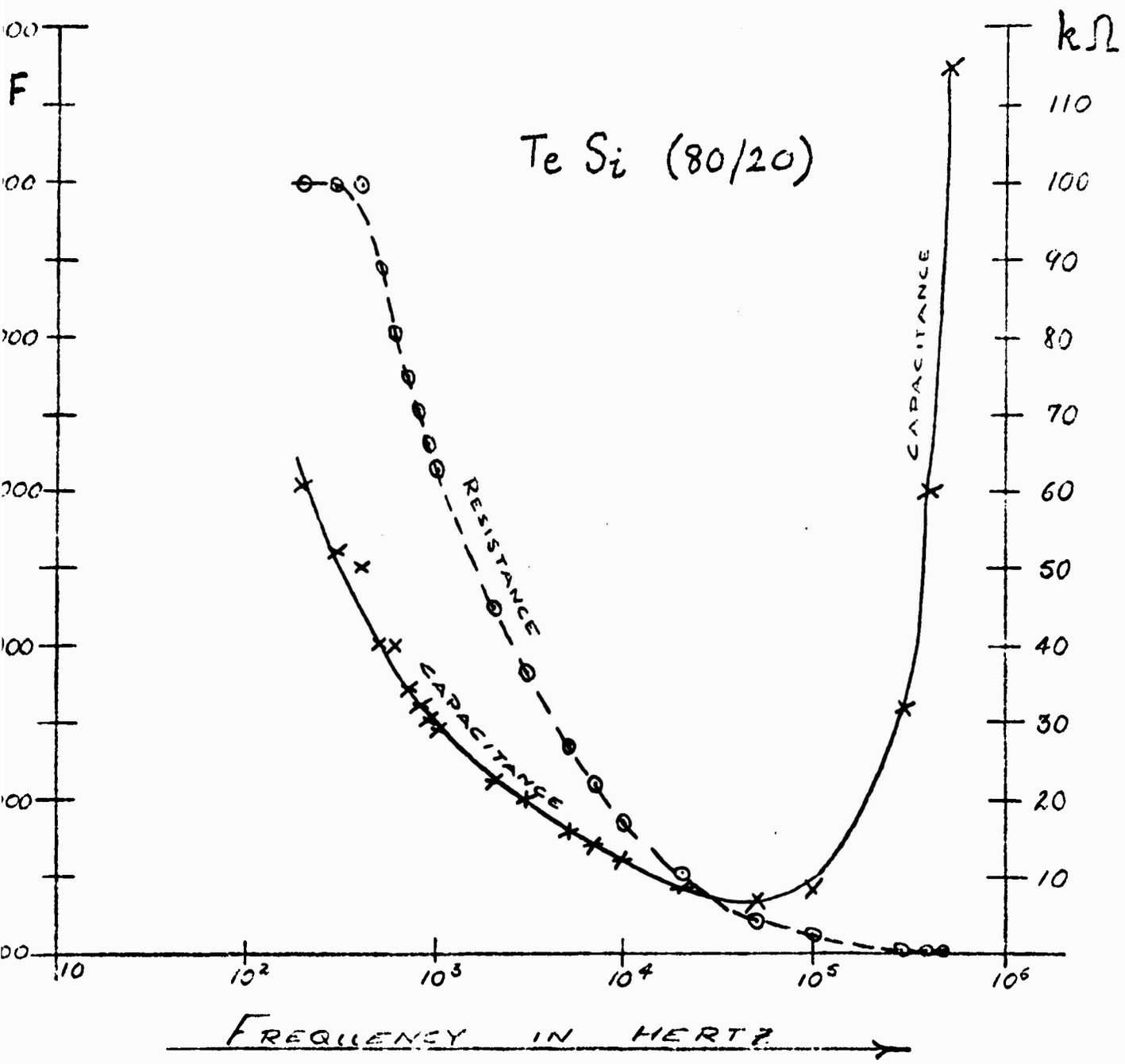
Te Si (80/20)
RESISTANCE
CAPACITANCE
CAPACITANCE
kΩ
110
100
90
80
70
60
50
40
30
20
10
10
10²
10³
10⁴
10⁵
10⁶
FREQUENCY IN HERTZ

Fig. 7

I-V Curve for a Thin Film GeTe Capacitor

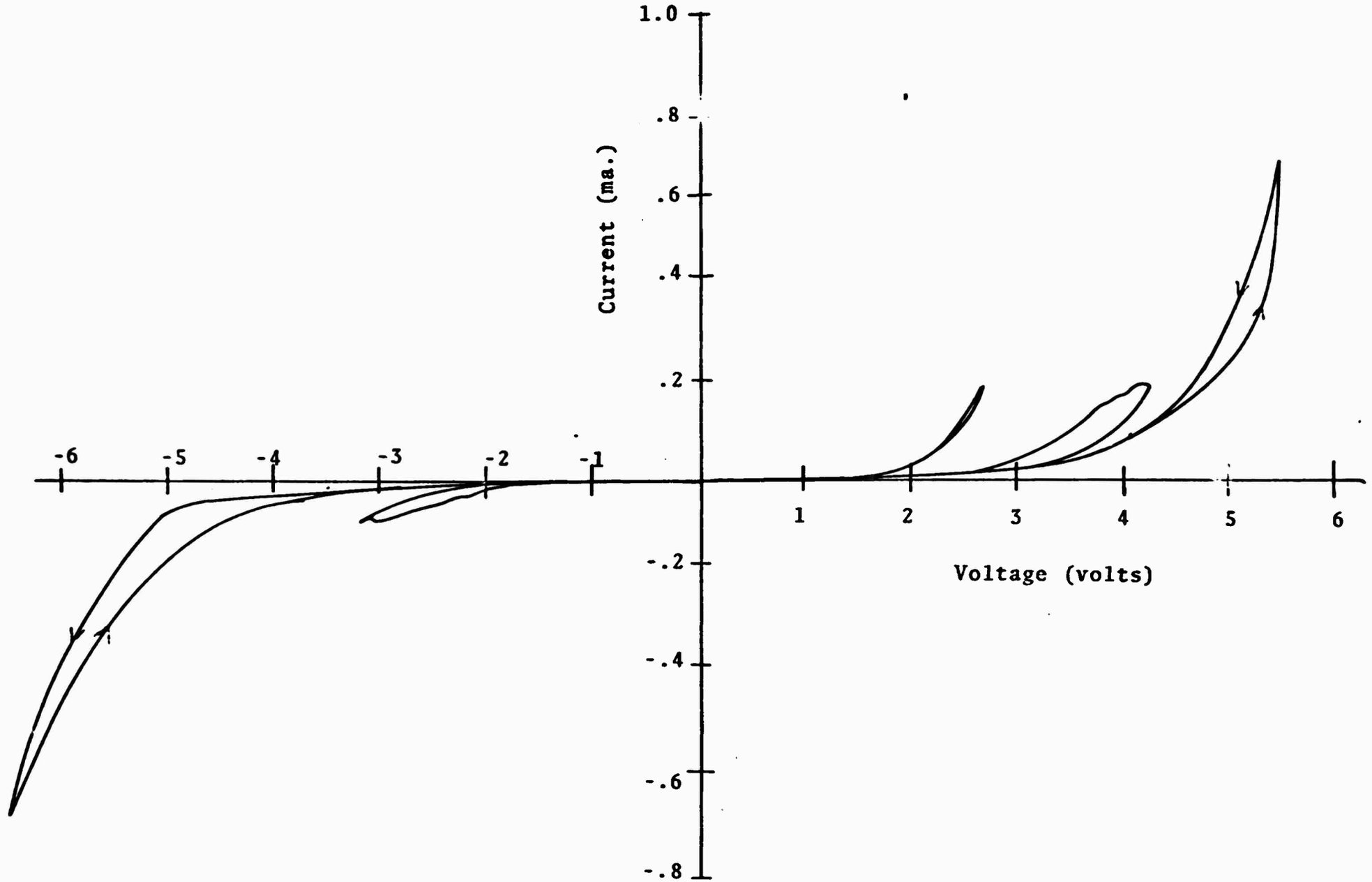

Fig. 8

Fig. 9a. Deterioration of Al electrode produced by tracing of iv curve in the non-linear region.

Fig. 9b. Electrode region of 9a showing collapse of blisters after insertion in vacuum.

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13. ABSTRACT

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Equipment for bulk glass preparation has been set up and some thin film structures have been fabricated by flash evaporation techniques. Work has commenced on local order structural measurements and electrical characterization of binary germanium tellurium alloys. It is intended that this study will be extended into more complicated systems as the project continues.

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