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CHARACTERIZATION OF "OPTICAL GRADE" GERMANIUM

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Philadelphia, Pennsylvania

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Various techniques were used to characterize "optical grade" germanium as to its suitability for optical element fabrication. Major concern centered about various material defects causing gradients in the refractive index and the need to detect these defects in germanium prior to its processing into optical elements. Cursory tests employing such methods as IR transmittance, x-ray radic aphy, x-ray topography and resistivity mapping were made on several germanium blank discs obtained from primary raw material suppliers.

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20. ABSTRACT - continued.
The tests indicated that these methods gave somewhat limited results and by themselves provided only a circumscribed characterization of the material.

A review of the literature on interferometry suggests that IR laser interferometry might be a promising quality assurance technique, although the extent of sample preparation for this technique may make its use too costly in any proposed quality inspection system.

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INTRODUCTION

Germanium is an attractive material for various infra-red optical components (e.g. lenses, windows, filter substrates) not only because of its inherent low optical absorption in the infra-red region but also because of the extensive commercial processing facilities that presently exist for this material.

Highly purified germanium that is destined for use in infra-red optical components is often referred to as "optical grade" germanium. At present the only specification for "optical grade" germanium is that its room temperature electrical resistivity be 40 ohm-cm. This specification is considered inadequate, however, by most users of optical grade germanium in that it does not reliably assess the optical quality of the material. A need therefore exists to further characterize "optical grade" germanium so as to better account for various "image-spoiling" factors not readily perceived by a determination of only the electrical resistivity of the material. Among such factors that need consideration are stress gradients and material inhomogeneities. This latter category includes small impurity concentration gradients as well as typical voids and inclusions.

With respect to characterizing voids and inclusions in order to assess the influence these defects would have on the image quality of infra-red optical elements, one can utilize existing specifications of optical transparent glasses.[1] However, major modifications to the techniques would need to be implemented before these specifications can be directly applicable to infra-red transparent germanium. With regard to stress and impurity gradients inducing excessive aberration in infra-red optical elements, far too little information presently exists in this area from which to draft an inspection procedure.

This report therefore describes the work that was undertaken to provide some information in this area. The objective of the work task was to investigate the capability of several material characterization techniques in detecting various image spoiling material factors in germanium.

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[1] Military Specification, MIL-G-174A

MATERIAL CHARACTERIZATION TECHNIQUES

"Optical grade" germanium discs nominally 2 1/4 inches in diameter and 1/2 inch thick were acquired from several primary raw material suppliers.[2] In most instances the germanium discs were examined in the "as received" condition with no additional sample preparation aside from a superficial etchant and/or solvent cleaning. Where appropriate the faces of the discs were optically polished by standard polishing techniques to give the faces a highly reflective surface.

Metallographic Examination

Several germanium discs were etched in a standard etchant (1 part H_2O_2 (30%), 1 part HF (conc.), 4 parts H_2O) to reveal the grain structure. Figures 1 and 2 are photographs of the etched faces of two representative specimen discs. They show the typical spectrum of grain sizes for a material that presumably originated from a zone refined ingot. All the specimens investigated were polycrystalline.

X-Ray Radiography

X-Ray radiography provides an effective means for non-destructively inspecting material for bulk defects. To evaluate the effectiveness of this technique for germanium, a sample disc was irradiated with x-rays generated by a tungsten target in a standard weld inspection unit. Several intentional defects were introduced into the specimen so as to assess the resolution capability of the technique. Figure 3 shows the location and type of defects introduced. The radiograph of the specimen is shown in figure 4. The intentional defects are readily discernable in the radiograph. No attempt was made in these tests to optimize the contrast nor improve the resolution capability of the technique.

Infra-Red Transmittance

The measurement of transmittance is a fundamental tool in the study of semitransparent material properties. It is often used to evaluate the optical constants of the material[3,4] or to determine the concentration of optically active impurities present in the host material.[5,6] As a method of characterizing "optical grade" germanium, transmittance measurements were performed on several uncoated germanium discs. The faces of

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[2]Eagle-Picher Industries Inc., GTE Sylvania Inc., & Exotic Materials Inc.

[3]Verleur, H. W., J. Optical Society of America, Vol. 58, p. 1356 (1968).

[4]Mc Carthy, D. W., Applied Optics, Vol. 2, p. 591 (1963).

[5]Briggs, H. B. and Fletcher, R. C., Physics Review, Vol. 91, p. 1342 (1953).

[6]Kaiser, W., et. al., Physics Review Vol. 101, p. 126, (1956).

the discs were optically polished to minimize surface reflection effects. No precaution was taken, however, to insure parallel faces on the specimens.[7] Measurements were performed on a Perkin-Elmer spectrophotometer Model 221. A typical transmittance spectrum is shown in figure 5. Different area scans on several different specimens gave basically the same spectrum. The spectrum agrees fairly well with those reported in the literature and is indicative of highly purified material.[8] The absorption occurring at 11.7 microns can be attributed to oxygen.[9] Standard ASTM procedures employing IR analysis are available to determine not only the concentration of oxygen present[10] but also identify several other impurity constituents that might be present in germanium.[11]

Electrical Resistivity

Impurities in germanium in general have an effect on electrical resistivity as well as optical transmittance. Electrical resistivity is a directly measurable quantity and standard ASTM procedures exist to measure electrical resistivity of semiconductor material by surface probe techniques.[12] One such ASTM procedure was used to obtain a surface resistivity mapping of a germanium disc. The mapping was performed on both faces of the specimen with a four point probe (probe spacing, 1 mm). Care was taken to define the location of the probe with respect to the grain structure of the specimen. Figures 6 and 7 show the surface resistivity values in ohm-cm superimposed on the grain structure of the faces. The probe unit exhibited good repeatibility and was calibrated with a single crystal silicon wafer of known resistivity.[13] Nevertheless, the resistivity values obtained have to be considered in relative terms rather than in absolute values since the four point probe technique is normally not recommended for polycrystalline material.[12] This is because localized impurity segregation at grain boundaries usually result in large resistivity variations. The higher than expected resistivity values observed for the sample are believed to be due to silicon impurity.[13,14]

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[7] LaBaw, K. B., et al., "Transmittance Measurements of Optical Materials as Affected by Wedge Angle and Refractive Index in the 2-15 Micron Range", U. S. Naval Ordance Test Station, Report #3116, April 1963, (AD 403 988).

[8] Moses, A. J., "Refractive Index Of Optical Materials in the IR Region", Hughes Aircraft Co., January 1970, (AD 704 555).

[9] Millet, E. J., et. al., British J. of Applied Physics, Vol. 16, p. 1593 (1965).

[10] ASTM Standard F122-70T, Interstitial Atomic Oxygen Content of Germanium by IR Absorption.

[11] ASTM Standard F120-70T, IR Absorption Analysis of Impurities in Single Crystal Semiconductor Materials.

[12] ASTM Standard F43-71, Resistivity of Semiconductor Materials.

[13] Private Communication, Mr. T. AuCoin, dtd. 9 Nov 73, U. S. Army Electronics Technology and Device Laboratory, U. S. ECOM, Fort Monmouth, N. J.

[14] Levitas, A., Physics Review, Vol. 99, p. 1810, (1955).

X-Ray Topography

X-ray topography is a useful non-destructive method for mapping microimperfections within the volume of a crystal. Near surface quality of the material (large grained or single crystal) can be examined by x-ray diffraction topography in the reflection mode (Berg-Barrett technique).[15] However, several criteria involving instrument resolution capability, specimen configuration and dislocation density level within the material must be met before direct observations of dislocations is possible. Furthermore, since the conditions giving rise to the contrast produced by dislocations in reflection topography are not clearly understood, finding no evidence of dislocations in the topograph is no assurance of their absence. Nevertheless, because of its relative simplicity, reflection topography is extremely useful in examining imperfections in the surface region. A reflection topograph was taken of a large grained region. This region is marked with an "X" in figure 1. The topograph is shown in figure 8. Twin boundaries and scratches are clearly evident in the topograph. The absence of many dislocations in the topograph can be partially accounted for by the fact that no special care was taken to obtain an appropriate internal reflecting plane in the grain so as to optimize dislocation viewing.

SUMMARY AND CONCLUSION

The various techniques that have been used to characterize the germanium samples have in general shown the material to be of sufficient high quality. No distinct areas of poor transmission were detected by infra-red transmittance nor did the cursory tests using x-ray radiography, topography and resistivity mapping reveal any unusual inhomogeneities that would degrade the image forming quality of the material. It should be noted, however, that all the tests were conducted on 2 1/4 inch diameter specimens. These specimens presumably originiated from similarly sized ingots. This ingot size is well established in the commercial crystal growing industry and therefore good quality control should normally be expected. For larger diameter material one may expect to find poor transmission areas due to the greater difficulty of establishing and maintaining uniform growth conditions in these larger sized ingots.

With the possible exception of x-ray topography, all of the techniques used could readily lend themselves to quality assurance inspection of supplier material. Some minimal preparation, however, may be needed to provide a surface more ammenable to inspection that the "as received" cut surfaces. Mass spectroscopic analysis is an additional technique worth considering to effectively determine impurity content.

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[15]Webb, N.W., Direct Observations of Imperfections in Crystals. Interscience, N.Y., J. B. Newkirk and J. H. Wernick Ed., p 29, (1962).

Since the ultimate objective is characterizing supplier material prior to undertaking optical element fabrication in order to detect inhomogeneities in the refractive index of the material, infra-red laser interferometry offers the most direct means of accomplishing this objective.[16,17] This technique has the ability to characterize refractive index gradients. At the same time the technique can also test for strain gradients, striae and inclusions. An apparatus using this technique is commercially available.[18] The major disadvantage with the technique, however, is that it is not specific to material inhomogeneities. Specimen flatness and parallelism will also influence the interferograms so that extensive sample preparation is necessary. This may prove too costly in any proposed inspection system.

In conclusion, several material characterization techniques can be adopted to provide quality assurance of germanium blank discs prior to optical element fabrication. One can expect, however, that any attempt to increase the sophistication of defect detection will correspondingly require greater sample preparation efforts. Nevertheless, IR laser interferometry appears to offer the most direct means for quality inspection of germanium not only at the start but throughout the optical element fabrication process.

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[16] Waugh, J., Optical Spectra. Vol.7 page 30 (June 1973).
[17] Rank, D. H., et.al., J. Opt. Soc. Amer. 44 page 13 (1954).
[18] Model IRI-10, Tropel Inc., Fairport, N.Y.

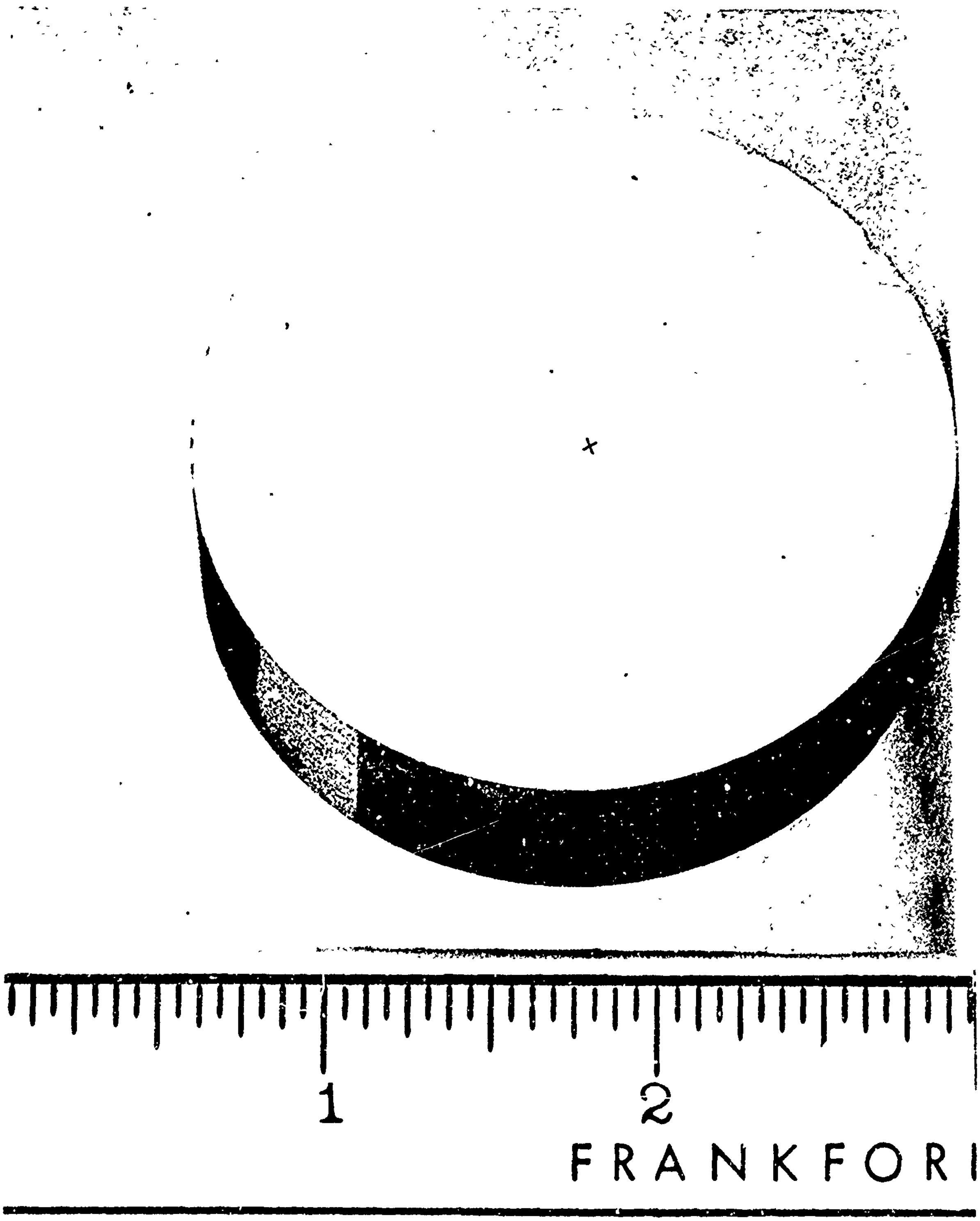

Figure 1. Grain Morphology of Germanium Disc, Specimen A.

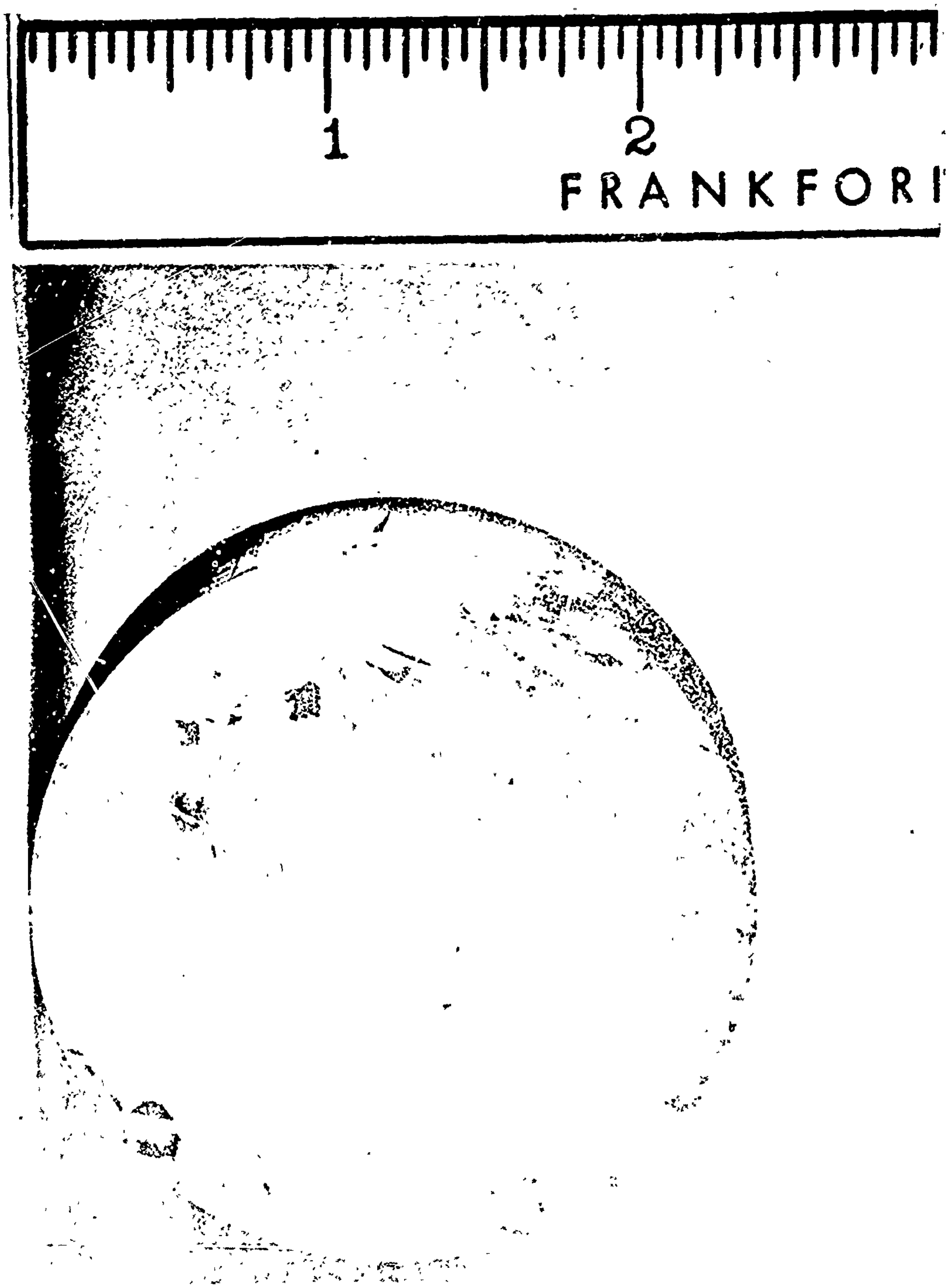

Figure 2. Grain Morphology of Germanium Disc, Specimen B.

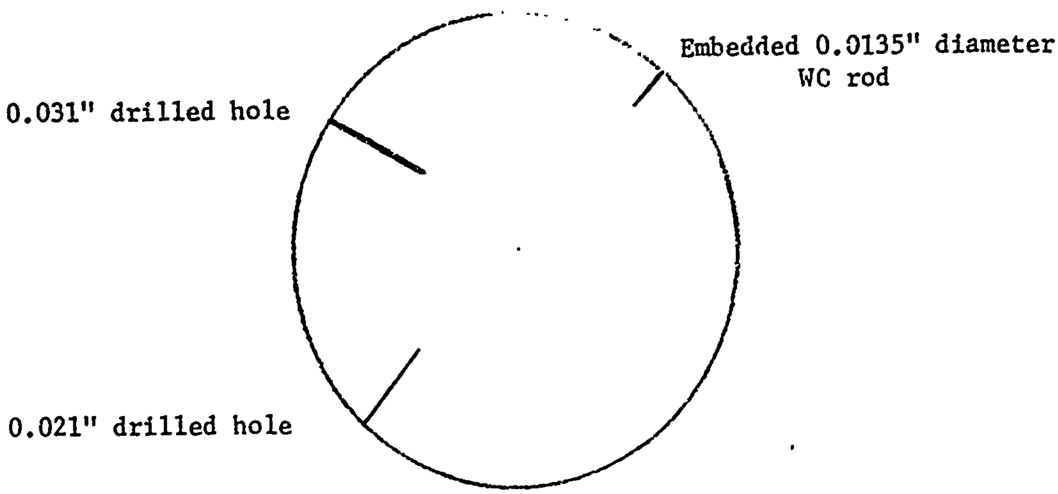

Figure 3. Radiographic Test Sample, Specimen B.

Figure 4. Radiograph of Germanium, Specimen B.

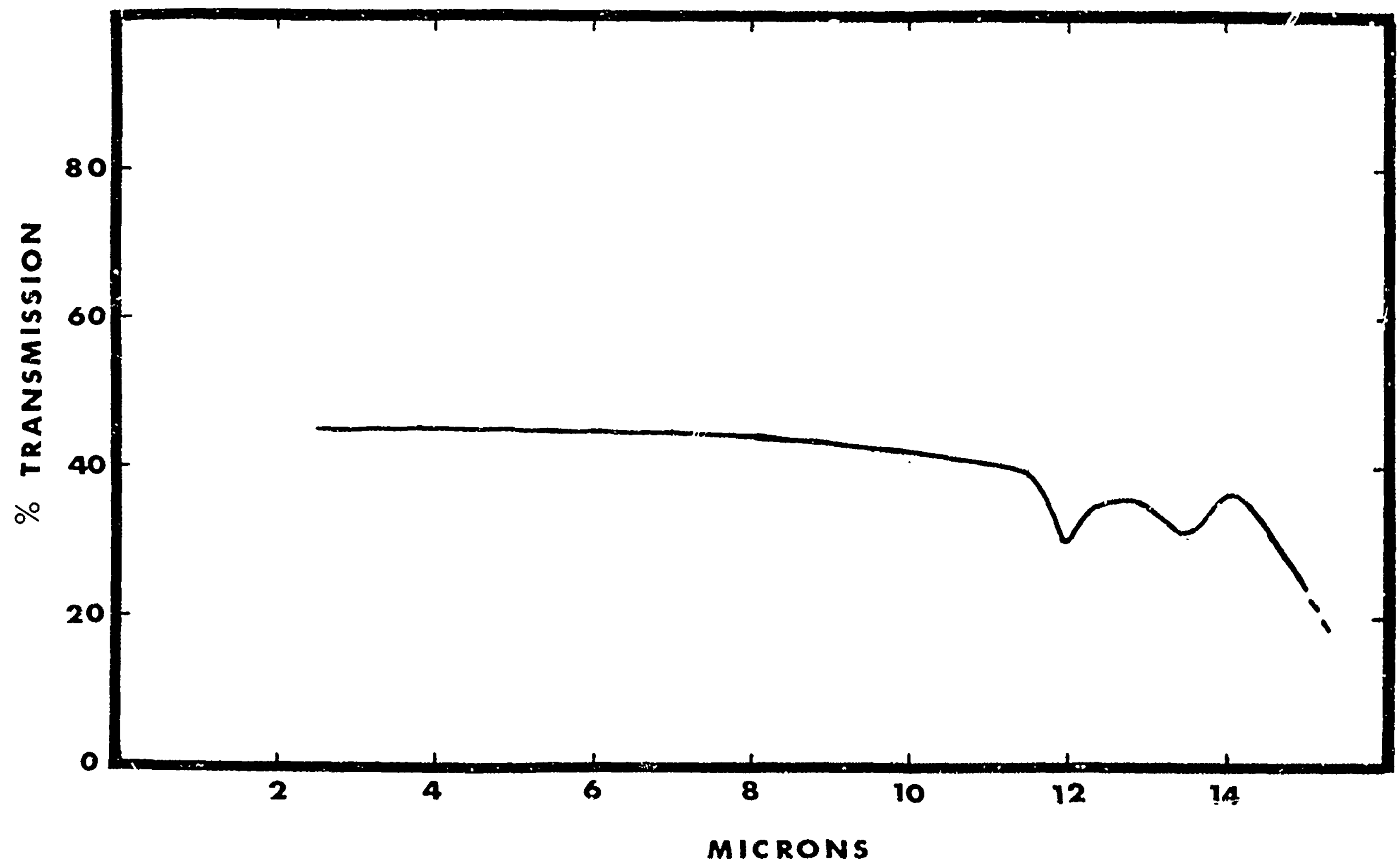

Figure 5. IR Transmittance of Germanium.

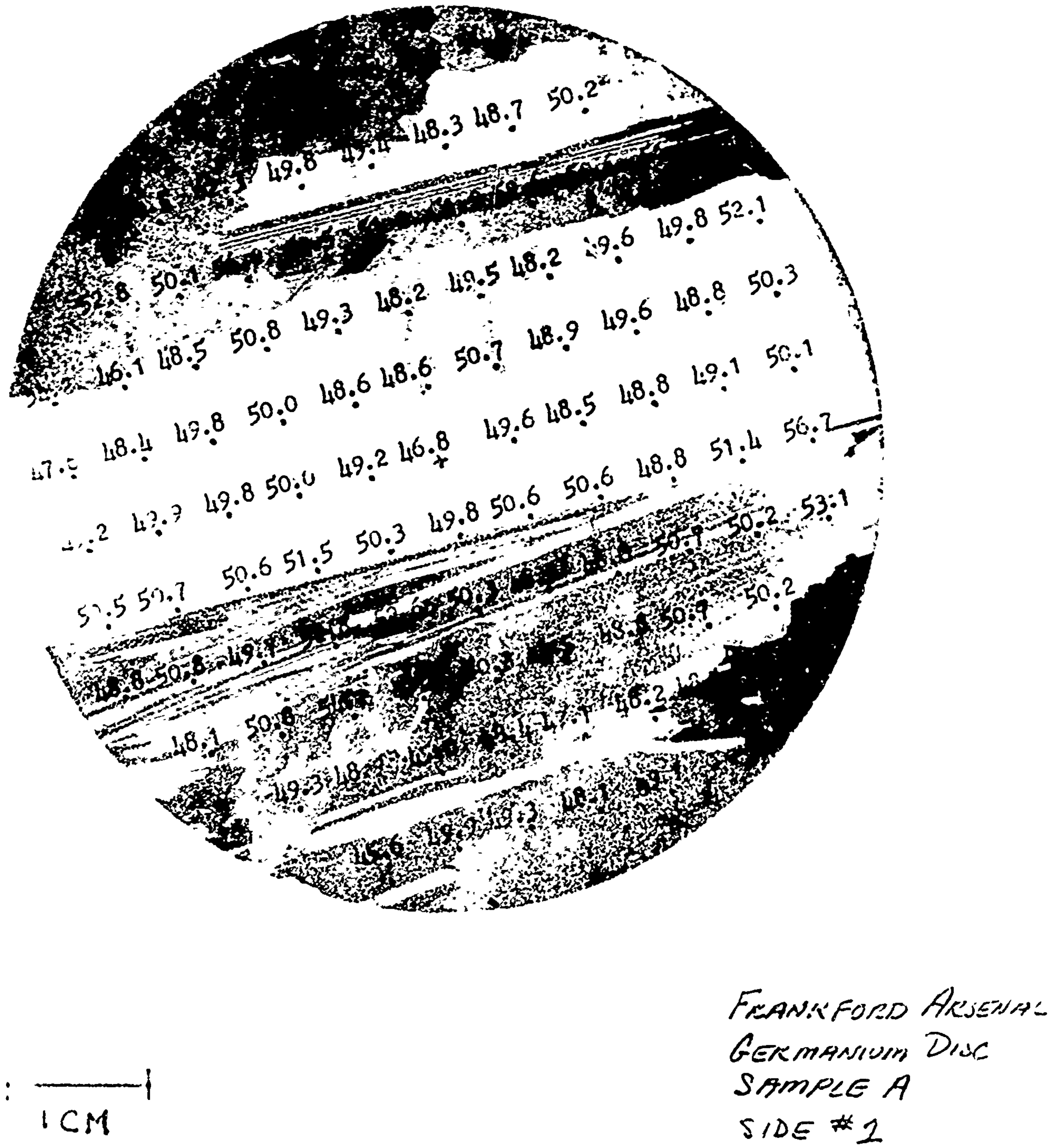

Figure 6. Surface Resitivity Mapping - Face 1, Specimen A.

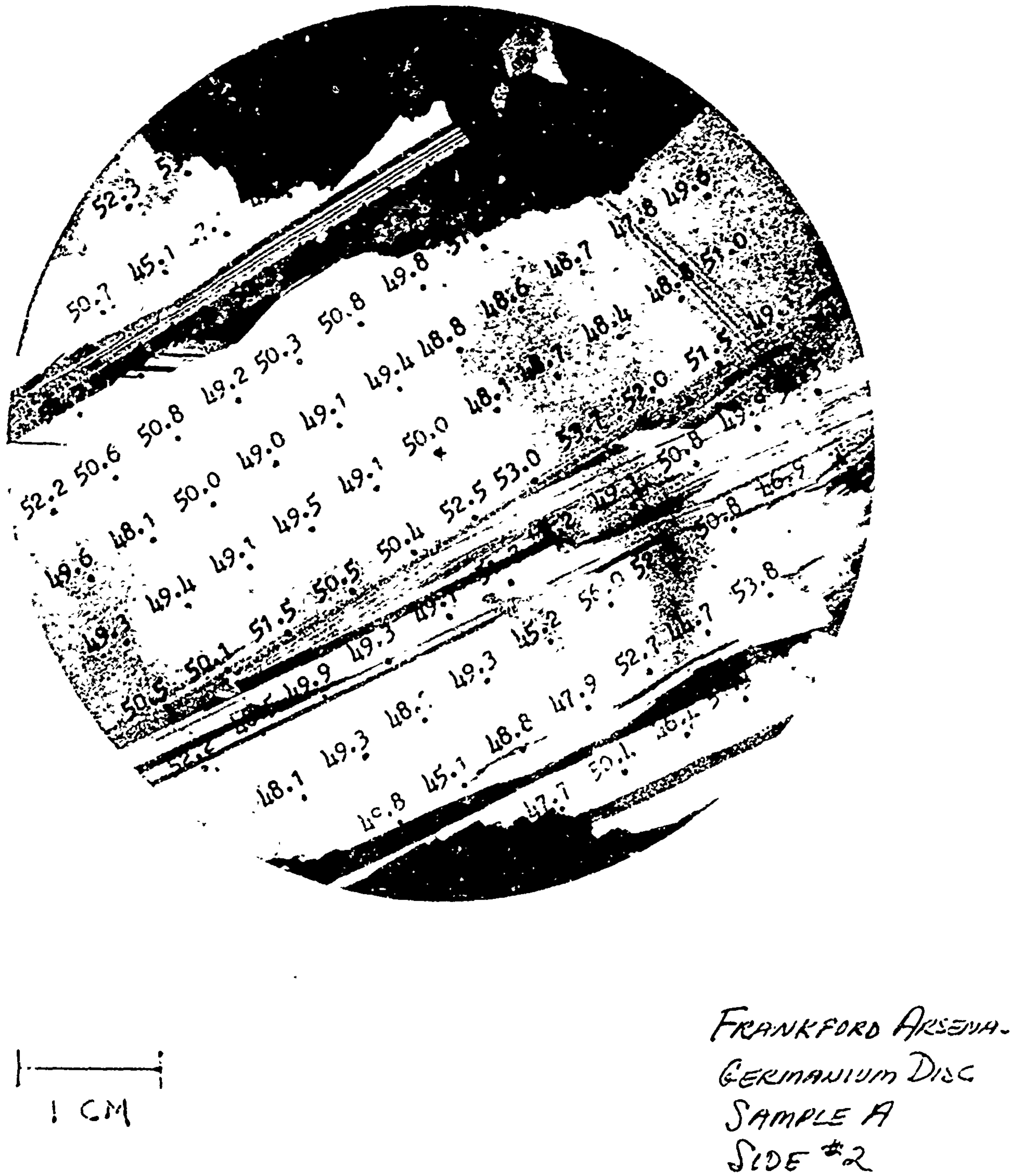

Figure 7. Surface Resistivity Mapping - Face 2, Specimen A.

Figure 8. X-Ray Topograph I, Specimen A.

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