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A SEMIANNUAL TECHNICAL REPORT

from

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Development and Application of SIMS Characterization Techniques
for the Study of Impurities and Impurity Motion in HgCdTe and CdTe

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OBJECTIVES

The broad objectives of this program are (1) to develop quantitative analytical procedures for the application of high performance secondary ion mass spectrometry (SIMS) to the analysis of CdTe and (HgCd)Te for trace element and major constituent characterization, particularly Hg, and (2) to perform materials-directed research in order to better understand the incorporation and redistribution of impurity elements in CdTe and (HgCd)Te. ←

PROGRESS SUMMARY

A. Analytical Procedures

1. Standardization

The major requirement for the quantitative analysis of impurity elements in CdTe and (HgCd)Te is the preparation of standards. Since SIMS is a relative technique, standards are prepared by ion implantation of the elements of interest into these matrices. The implants are being made under a subcontract to Dr. Robert Wilson of Hughes Research Laboratories, Malibu, CA.

In our initial attempts to depth-profile implants in CdTe, we encountered serious problems due to electrical charging under ion bombardment. Thus, these samples have been set aside until we can develop procedures to counteract charging effectively. (This topic is discussed in detail below.)

Other implants were prepared in (HgCd)Te. Since the implantable area of material available to us is small, Dr. Wilson implanted several ions into each sample. Depth profiles of the ions in these multiple-implanted samples had peculiar distributions, suggesting some difficulty with the (multiple) implantation into (HgCd)Te. No such effect was observed in depth profiles of similar species implanted together in Si, Ge or GaAs. Work is in progress to resolve this issue.

2. Mass and Energy Spectra

In the past six months, we have focussed on many preliminary aspects of analytical procedures development. Complete secondary ion mass spectra have been acquired from the II-VI compounds CdTe, (HgCd)Te, (ZnCd)Te and (MnCd)Te. These spectra were acquired using positive secondary ion spectroscopy (facilitated by O_2^+ primary ion bombardment) and negative secondary ion spectroscopy (performed by Cs^+ primary ion bombardment). Further, the effect of secondary ion initial kinetic energy discrimination was studied. Initial kinetic energy distributions were obtained for major constituents and for some doubly-ionized atomic ions and molecular ions.



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The mass and energy spectra enabled the identification of the major spectral interferences in these matrices and the development of standard operating conditions to minimize the effect of spectral interferences. On the basis of these spectra, it became apparent that in Cd-bearing telluride compounds the matrix ion of choice for normalization should be $^{125}\text{Te}^{\pm}$ and not the ion of the major isotope $^{130}\text{Te}^{\pm}$ as had been previously used. Cadmium oxide molecular ions can "contaminate" the other major tellurium isotopes.

The most fruitful studies in this series were those on the initial kinetic energy distributions of the secondary ions emitted from the sputtered matrices. For most secondary ions, whether matrix level or impurity, the initial kinetic distributions begin at or near zero and extend over a range to higher initial kinetic energies. The width of this distribution is generally greater for singly and multiply-charged ions than for multi-atomic, molecular ions. We routinely take advantage of this phenomenon by using the voltage offset mode of SIMS, a technique which limits measurement to ions in a selected energy range. This process is used to reduce spectral interferences due to molecular ions with the same mass as the atomic ions of analytical interest. Generally, this technique is not as effective against interferences from multiply-charged ions, a dominant spectral problem in (HgCd)Te and CdTe, particularly multiply-charged Cd, Te and Hg at the masses of the transition elements.

Our results on the initial kinetic energy spectra of ions sputtered from these II-VI compounds provide essential, independent corroboration of important initial observations by Holland and Blackmore (1982).^{1,2} Unlike any other elements we had studied, the singly-charged Hg ion and multiply-charged ions of Cd, Te, Hg and Zn had kinetic energy distributions with little or no ions above zero eV initial kinetic energy. The energies of these ions begin at zero eV and are distributed over a range of energies extending significantly below zero. By recognizing that the multiply-charged matrix ions in CdTe and (HgCd)Te have "retrograde" energy distributions, we can use the voltage offset technique, not normally effective for multiply-charged ion interferences, to increase the signal to interference intensity ratio and thus greatly improve our detection limit for several of the transition element species.

In an effort to clarify the origin of such unusual secondary ion distributions, our measurements went beyond previous work to include Cs^+ and O^- ion bombardment, as well as O_2^+ ion bombardment. We observed that the ion yield versus energy of the singly-charged matrix species varies linearly with bombarding ion current density in the region of the energy spectrum from zero eV and up, regardless of bombarding species. (No results were obtained for Cd and Hg under Cs^+ bombardment since they do not form negative ions). The most significant observation was that in the region of the energy spectrum from zero eV and down, the ion yield of Hg^+ , Cd^+ and Te^{2+} vary quadratically with bombarding ion current density. The effect is shown as ion yield curves versus energy for Hg^+ , Cd^+ and Te^{2+} in Figures 1-3, respectively.

These studies indicate two causes for the irreproducibility of Hg^+ intensity measurements in previous studies.

As seen in Figure 1, the Hg^+ ions are mostly distributed at kinetic energies at or below zero eV, with a small number of ions appearing at zero and greater kinetic energies. Analysis of most species require the spectrometer to be set to accept ions of zero and greater kinetic energies. This fact, coupled with the commonly encountered electrical charging under ion bombardment which causes irreproducibility shifts in the entire energy spectrum of Hg, results in the poor reproducibility of mercury analyses. Secondly, Hg^+ ion production over most of its energy distribution depends quadratically on the bombarding ion current density, which unlike the ion current, is difficult to reproduce from day to day.

Thus, by purposely setting the instrumental parameters to efficiently collect the zero-and-below kinetic energy ions of Hg^+ , and by dynamically compensating for charging, we measure a more constant Hg^+ ion intensity. In combination with tight control on the instrument parameters governing bombarding current density, we expect to realize a return in much improved sample to sample reproducibility for Hg analysis.

3. Data Acquisition and Presentation

To some extent, implementing the above procedures to achieve improved analytical capabilities requires the application of novel data acquisition and presentation techniques in our analyses of these materials. These allow easier access to and better control over the considerable amount of information contained in a depth profile.

Control software has been developed to exploit the Cameca IMS-3f instrumental capability for determining the extent of sample charging during profiling of epitaxial layers. Charging can be compensated dynamically and a plot of voltage compensation versus depth prepared. This gives a valuable insight into the extent of charging during profiles of epitaxial layers on semi-insulating substrates, or any other structure. Thus, we can isolate artifacts which might relate to sample charging.

At the completion of each analysis, we can evaluate the total integrated counts for each impurity with matrix normalization. This is a quality-control feature which allows real-time comparison of experimental data with expected behavior or with other data.

Other routines can be used to prevent the very intense matrix ion signal from saturating the sensitive electron multiplier detector as the spectrometer magnet slews from impurity mass to impurity mass. This prevents a variable detector gain which manifests itself as instabilities in the ion intensities recorded for the species immediately beyond the intense matrix ion signal. Additionally, intensity versus depth data for selected matrix ions can be presented on linear scales, which helps to more closely monitor the variations in compound stoichiometry.

4. Materials Research

This phase of the research involves our collaboration with other research groups which specialize in materials growth and preparation. During this period we performed three materials related studies, with varying success, depending on the analytical behavior of each sample type.

We were provided a bilayer slider-grown LPE (HgCd)Te sample by the group under R.A. Wood at Honeywell, Minneapolis, MN. This sample was prepared so that there was a deliberate variation in X, the atomic fraction of Cd. We did not observe the growth variation when the sample was profiled using SIMS, but this work was done prior to the above-mentioned fundamental Hg studies. Therefore, armed with our new knowledge we will remeasure the sample and report the results at a future date.

Some cast CdTe was provided to us by Dr. R. Hilton of Amorphous Materials, Inc., Garland, TX for general examination and preparation suitable for ion implantation. This material provided most of the mass spectral data for molecular interferences and remains quite useful for a variety of purposes. Several pieces are being polished for ion implantation by the proprietary "hydroplaning" operation by Dr. T. Magee of Aracor, Sunnyvale, CA. We hope to report the progress on that aspect soon.

In collaboration with Prof. J. Schetzina of North Carolina State University, Raleigh, NC, we have applied SIMS to a variety of MBE grown CdTe layers on (HgCd)Te, InSb and sapphire substrates. The quality of this CdTe was very good and its semi-insulating properties made the analysis difficult. Some of the samples were sufficiently insulating to preclude analysis under positive ion bombardment. We are now planning repeating these analyses with gold coating and negative ion bombardment. The data from those that were analyzable is now being reduced and evaluated. These results will be reported in a future communication.

5. Significant Problems/Future Work

The greatest problem encountered during the initial analysis of these materials by SIMS was that of surface charging under ion bombardment. Except for epitaxial (HgCd)Te, all substrate and bulk CdTe, ZnCdTe, MnCdTe, etc., exhibited moderate to severe electrical charging. We anticipate that the next phase of our research will focus on this issue.

Several strategies, successfully employed in the past for analysis by SIMS of electrically insulating samples, are available. We anticipate studying the effects of:

- a. sputter-coating the samples with a conductive film

- b. simultaneous bombardment of the sample surface with an electron beam (during O_2^+ bombardment)
- c. using a Mo aperture placed over the areas of analytical interest
- d. use of O^- oxygen bombardment
- e. preparation of ion implants in electrically doped substrates as possible means to overcome the problem.

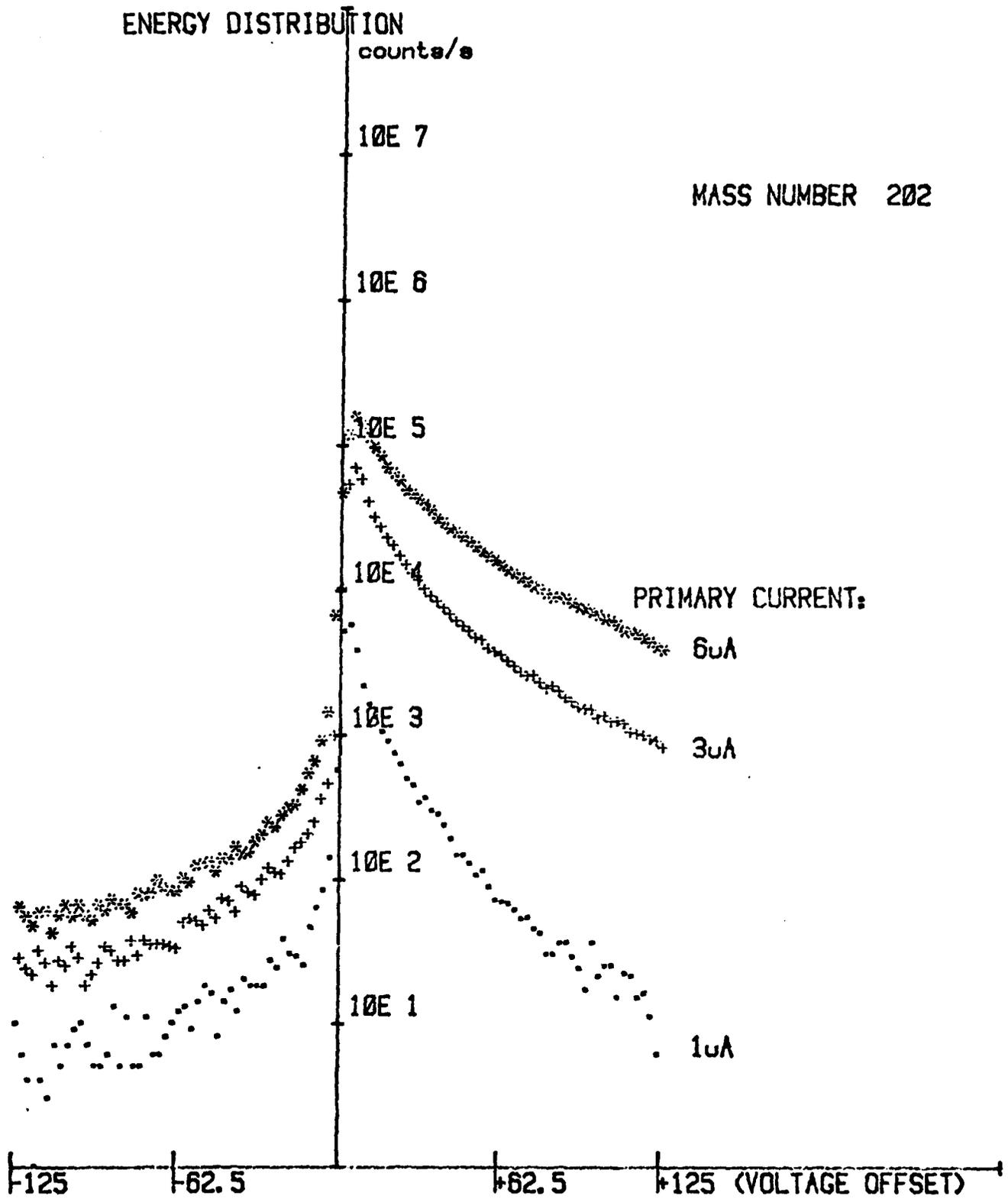


FIG. 1 Hg^+ ION INTENSITY VS INITIAL KINETIC ENERGY FOR SEVERAL PRIMARY ION CURRENTS

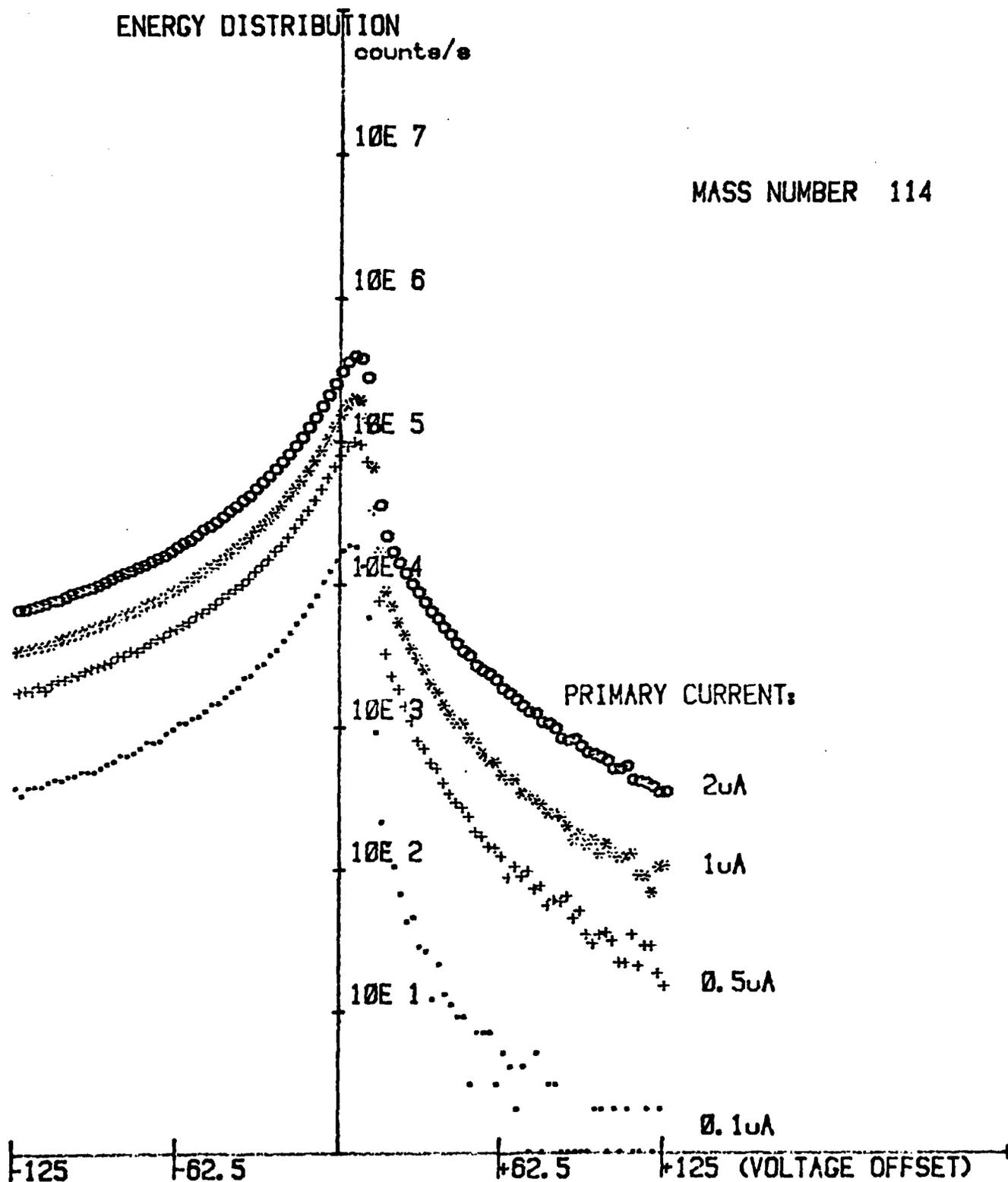


FIG. 2 Cd+ ION INTENSITY VS INITIAL KINETIC ENERGY FOR SEVERAL PRIMARY ION CURRENTS

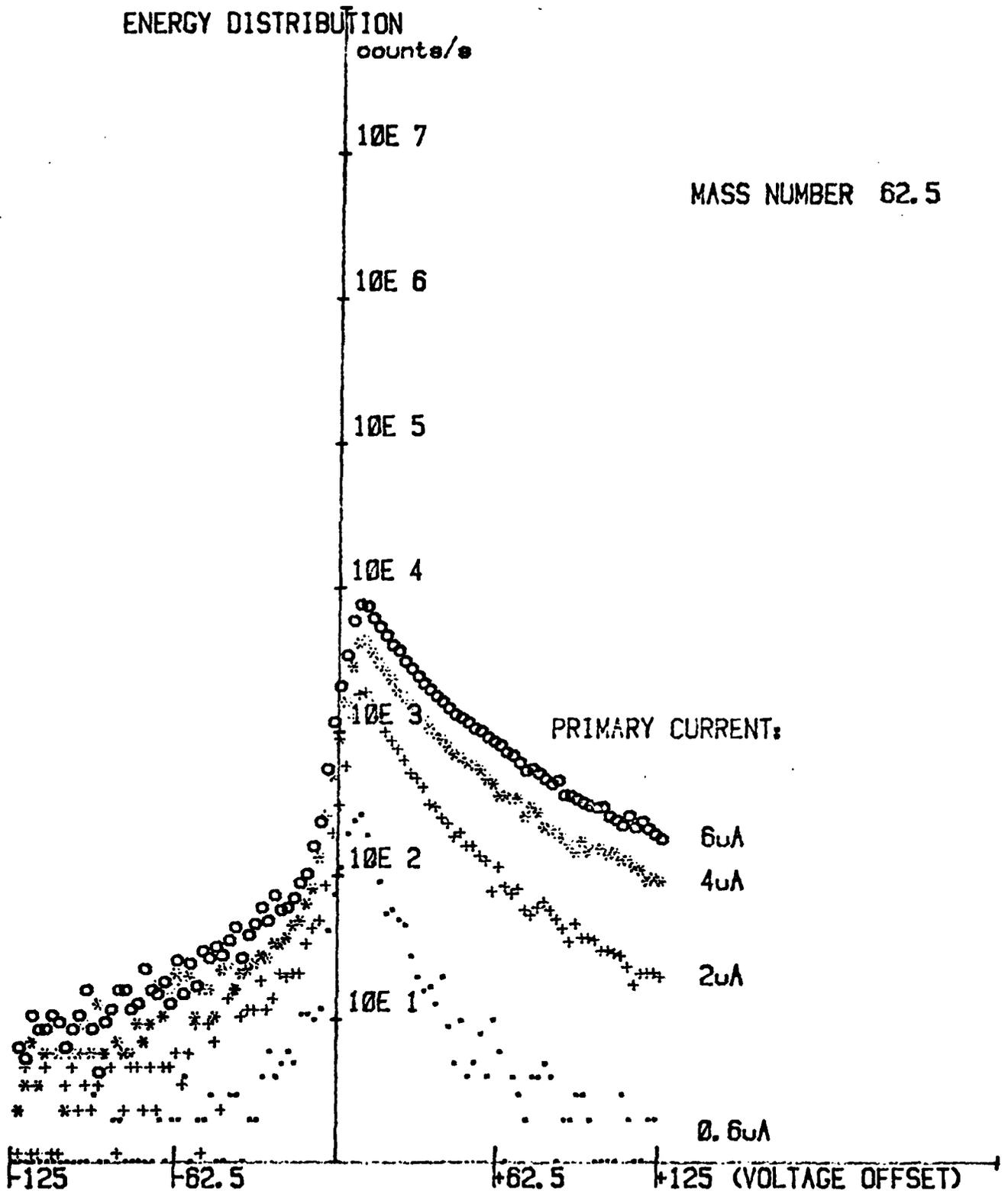


FIG 3. T_2^{2+} ION INTENSITY VS INITIAL KINETIC ENERGY FOR SEVERAL PRIMARY ION CURRENTS

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DESCRIPTOR SET

(U) *MANUFACTURING, *ARMY EQUIPMENT, *ARMY OPERATIONS, *LOGISTICS SUPPORT, PRODUCTION, METHODOLOGY, PLANNING PROGRAMMI
NG BUDGETING, REPORTS, OPERATIONAL READINESS, TABLES(DATA), COMPUTER PRINTOUTS
ABSTRACT

(U) THE BROAD OBJECTIVES OF THIS PROGRAM ARE TO DEVELOP QUANTITATIVE ANALYTICAL PROCEDURES FOR THE APPLICATION OF HIGH
PERFORMANCE SECONDARY ION MASS SPECTROMETRY (SIMS) TO THE ANALYSIS OF CDTE AND (HGCD) FOR TRACE ELEMENT AND MAJOR CONS
TITUENT CHARACTERIZATION, PARTICULARLY HG, AND TO PERFORM MATERIALS-DIRECTED RESEARCH IN ORDER TO BETTER UNDERSTAND THE
INCORPORATION AND REDISTRIBUTION OF IMPURITY ELEMENTS IN CDTE AND (HGCD)TE.

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