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SPACE PROCESSING OF CRYSTALLINE MATERIALS: A STUDY OF KNOWN METHODS OF ELECTRICAL CHARACTERIZATION OF SEMICONDUCTORS

by

J. G. Castle

Final Technical Report

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FINAL TECHNICAL REPORT ON CONTRACT NAS8-30774

TITLE OF CONTRACT: Space Processing of Crystalline Materials: A Study of Known Methods of Electrical Characterization of Semiconductors

ABSTRACT: A literature survey is presented covering nondestructive methods of electrical characterization of semiconductors. A synopsis of each technique deals with the applicability of the techniques to various device parameters and to potential in-flight use before, during, and after growth experiments on space flights. It is concluded that the very recent surge in the commercial production of large scale integrated circuitry and other semiconductor arrays requiring uniformity on the scale of a few microns involves nondestructive (optical ?) test procedures which could well be useful to NASA for in-flight use in space processing; these methods have apparently not yet been described in detail in the open literature.

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Foreword

For an extensive search of the technical literature, the author owes special thanks to Michael Valpiani, who as an undergraduate physics major at UAH displayed enough enthusiasm to get us both through the high volume filtering opration required, especially for the infrared and optical scanning techniques. It is hoped that the selection presented in the attached bibliography will be a useful one.

For an epilogue, the summary can hardly do justice to the need for the NASA staff to obtain up-to-date details from the semiconductor manufacturers or their users as to the scanning techniques employed with recent successes in such diverse applications as LSI, CCD, LED, LSA diodes, etc. With some of the specifics, a realistic estimate of utility of scanning semiconductor during growth in space can be made and a ground-based adaptation tested in time for Spacelab.

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SPACE PROCESSING OF CRYSTALLINE MATERIALS: A STUDY OF KNOWN METHODS FOR ELECTRICAL CHARACTERIZATION OF SEMICONDUCTORS

I. INTRODUCTION

Several Skylab crystal growth experiments attained semiconductor crystals of significantly higher quality than has been attained by the best growth techniques on earth. The potential for higher uniformity of semiconductors grown in space on such extended missions as Spacelab offers significant advantages to several kinds of semiconductor manufacturing. For example, one advantage of better uniformity is higher density arrays on semiconductor chips, the value of which can be illustrated by the recent reduction by a factor of two in the cost of semiconductor memory chips for hand calculators when the optical processing permitted the decrease in spacing of elements from 5 microns to 4 microns on silicon chips.

Effective development of crystal growth techniques in the microgravity of space flight will require specific adaptation of nondestructive methods for characterizing the electrical properties of the semiconductor crystals, either during or promptly following their growth. Automated nondestructive scans of the surfaces of the semiconductor sheets grown in space for nonuniformities in the appropriate electrical/optical parameter(s) can be developed and their use in space processing would make real-time feedback possible during crystal growth. Significantly better crystal quality would then be expected.

The role of this short study of methods of electrical characterization of semiconductors is to search the open literature for recent advances in experimental technique which would appear to be applicable to the space processing of semiconductors. The form of the results is an extended bibliography, organized around synopses of the types of measurements. Emphasis in the discussions summarizing the applicability of the published information to the space processing of semiconductors is strongly toward those methods which are capable of high resolution noncontacting characterization. Unfortunately no published description of an operational high resolution noncontacting technique was found, in spite of plenty of evidence in the trade journals that such scanning techniques are in use by manufacturers, at least in a semiautomatic form.

Electrical characterization of a semiconductor crystal grown for a particular device application will require measurement of certain electrical parameters of the semiconductor. In general, the characterization will require the nondestructive measurement of one or more of the following parameters:

1. Resistivity, ρ.
2. Densities of charge carriers, N_e and/or N_h.
3. Densities of various impurities. The four principal categories of interest being donor or acceptor centers forming deep or shallow traps. In the compound semiconductors, a larger variety of active centers is of interest in many of the modern device applications.
4. Mobility of each of the active carriers, μ_i.
5. Lifetimes of the active carriers, τ_i.

An attempt has been made to organize the attached bibliography around these five electrical parameters. Special applications cften require characterization of special parameters not included above. For example, light-emitting diode (LED) performance is affected not only by the above five parameters but also by such special parameters as light-scattering and internal strain fields. For an example in the field of cooperative effects, useful diode devices depend on the nonlinear response of the semiconductor, e.g. the strength of the Gunn effect depends on the mobility having a dip (a region of negative slope) with respect to applied field strength. It was beyond the scope of this limited study to include many of these special cases. It should be noted, however, that NASA's space processing of semiconductors may well have its largest impact in the special applications where high uniformity may bring the largest advantages.

In order to exemplify the whole range of semiconductors, we cite the methods reported for characterizing the following materials:

Silicon - for the elemental semiconductors.

Gallium Arsenide - for the III-V compounds.

Cadmium Sulphide - for the II-VI compounds.

Silicon has been the material of choice for decades for transitors, and still is for the arrays of diodes and transitors called integrated circuitry. Solar cells, semiconductor memories, and charge-coupled devices (CCD's) are usually made of silicon also. Unwanted impurities and crystal defects are kept down in concentration to levels as low as a few parts per billion in high performance devices, where the carrier density is typically 10 to 1000 ppm.

Uniformities required range around a few percent variation to a fraction of one percent variation averaged on a scale of dimensions appropriate to the device application. Clearly, for a transistor on an LSI chip, the local values of the above parameters are what count, so characterization needs to measure averages over the size of the transitor - say from a micron to tens of microns in lateral dimensions across the surface to be used. Similar scale applies to CCD's and other semiconductor memories.

A different scale of characterization applies to large area photocells, such as solar cells, whether they be of silicon or cadmium sulphide or gallium arsenide material. In solar cells, the critical dimension is the depth within which the junction is to be formed; recently, violet solar cells have been successfully operated with junction depths as small as 0.1 microns (1000 Å), but lateral uniformity of carrier mobility is still required in order for the carriers to be collected by the metal grid.

An instructive example of how nonuniformity in electrical characteristics affects a device adversely is in an image sensing array of phototransistors. A photosensitive junction field-effect transitor located on the chip surface at each of the resolved elements of the image offers the considerable advantages of gain and storage with nonerasing readout. If each JFET has the same response to a given light exposure, useful image detection occurs with high sensitivity. However, variations in dopant and in thickness of the IC epilayers make for difficulty in attaining useful uniformity except at low sensitivity. A recent issue of ELECTRO-OPTICAL SYSTEMS DESIGN notes a mode of operation of such a JFET array demonstrated by A. Schmitz and F. Smolders of the Phillips Research Labs, Eindohoven, Holland, in which at least the threshold voltage variations can be compensated for in binary operation of each JFET, area ~ 1500 micron^2. Wide use of these arrays awaits uniformity improvement.

II. CATEGORIES OF METHODS OF ELECTRICAL CHARACTERIZATION OF SEMICONDUCTORS

A. Nondestructive Coupling to the Semiconductor

For a method of characterization to be fully effective in on-line quality control in semiconductor manufacturing, whether on the ground or during space processing, the method must involve a noncontacting technique for scanning the semiconductor surface and, for most applications, noncontacting means of readout. Such a combination allows complete scanning for nonuniformities without inducing imperfections into the high quality semiconductor.

An exception should be noted for the class of applications in which large area electrodes are to be affixed to the semiconductor. An important member of this class is the planar photodiode, used as a solar cell or as a solid state photomultiplier. The noise in "ordinary" boron-diffused P+NN+ planar avalanche diodes manufactured on high-quality silicon is due to dopant fluctuations in the photosensitive area of typically 10%. Recently, the Phillips Research Laboratories used ion implantation to get dopant fluctuations down to 0.1%; L. Bollen of Phillips is reported in Electro-Optical Systems Design, January 1975, to have characterized the photoresponse of these more uniform diodes by means of a flying-spot microscope and found more uniform photoresponse and the noise to be mainly shot noise, just as in a vacuum photodiode. Flying spot scanners are available with spot sizes down to a few microns.

The requirements of noncontacting scanning and noncontacting readout can be satisfied only by coupling to the semiconductor by high frequency radiation - Microwave, Infrared and Optical Categories in the matrix below - and by ionizing radiation. The latter is not included in this survey because of its destructive influence on the semiconductor being characterized. The low frequency methods - DC and Radio Frequency Categories - are included in the matrix below in spite of their normal requirement of soldered contacts and cut samples because they yield the bulk average values for the electrical parameters normally used as procurement specifications for semiconductor material; but the low frequency methods are not considered candidates for the scanning techniques required to characterize the degree of nonuniformity. The preferred low frequency method of obtaining bulk resistivity nondestructively is loading of an rf coil by the semiconductor boule or sheet.

The minimum size area of the semiconductor surface that can be nondestructively sampled is given by the Airy function for a multimode optical system; the minimum diameter is approximately the product of the wavelength, λ, times the f-number of the optical system. For a single mode pattern incident on the semiconductor surface, such as on the wall of a resonant cavity, the minimum dimensions are of order $\lambda/2$, with the option of proportionately reduced sensitivity when the area of the semiconductor surface being sampled is reduced below dimensions of $\lambda/2$. So microwaves at 35 GHz can sample nondestructively areas measuring a few millimeters across, and optical methods work in the resolution range of a few microns. It should be noted that optical scanning and microwave readout can give the characterization of the optical spot size in some cases.

In any case, it takes an optical technique to characterize the uniformity of the electrical characteristics of high quality semiconductors on the scale of dimensions important to most of today's semiconductor applications.

F. Matrix of Categories of Methods vs. Scale of Resolution

Historical labels are often useful in identifying electrical effects in semiconductors. The effects can be measured in a variety of ways. For the purpose of this review, the ways of measurement are grouped by frequency of the radiation being used to perturb the semiconductor and to readout its response to that perturbation. It is convenient to arrange the methods being reviewed in the matrix in Table 1.

Each reference cited in the attached bibliography is labeled by the abbreviations for the electrical parameter(s) and the frequency range employed. In the next section, brief synopses are given for each of the above methods, starting with the low frequency ones and ending with those methods with the greatest potential utility to NASA's space processing of crystals of semiconductors.

TABLE 1. METHODS OF ELECTRICAL CHARACTERIZATION OF SEMICONDUCTORS

Grouping by electrical parameter and by the frequency of radiation used to couple to the semiconductor corresponds to the sequence of the discussion in the text. Solid underline indicates both noncontacting scanning and noncontacting readout; dashed underline indicates noncontacting scanning. The sense of scanning with coil loading is to load the coil with several diameters length of a boule or a limited area of a sheet of semiconductor.

RADIATION FREQUENCY (Abbreviation) →	LOW (DC to RF)	MICROWAVE (MW)	INFRARED AND OPTICAL (IR & OP)
Sampling Average →	Bulk of Crystal	Surface within Skin Depth, δ	
Resolution Size →	Bulk	1 mm	500 to a Few Microns
ELECTRICAL PARAMETER (Abbreviation) ↓			
Resistivity, ρ (RHO)	Bulk Resistance by van der Pauw Coil Loading (Skin Effect)	Surface Resistance (Skin Effect)	
Mobility, μ (MU)	Hall Effect	Hall Effect Faraday Rotation	Faraday Rotation
Differential Mobility, $d\mu/dE_{app}$ (DMU)	Gunn Effect	High Field Permittivity	Differential Photovoltage
Carrier Lifetime, τ (TAU) and/or Density of Impurity, N_i (IMP)	Skin Effect Anomaly	Electron Spin Resonance Cyclotron Resonance	Photovoltage Photoinduced Conductivity Photoluminescence Photon Absorption

III. REVIEW OF METHODS OF ELECTRICAL CHARACTERIZATION

Each of the methods listed in the matrix above is reviewed. Following each synopsis, the pertinent references in the bibliography are listed by the first three letters of the author's name and the year of publication.

A. Low Frequency Methods, DC to RF

The only one of the low frequency methods which is sufficiently non-contacting to serve to obtain quasibulk averages without damaging high quality semiconductor crystals is coil loading. The high local pressure of movable probes is probably more damaging than some soldering techniques.

1. Bulk Resistance

Samples of regular geometry are usually cut from the semiconducting boule to be characterized, although van der Pauw's method of averaging permits the use of irregular shapes if a sufficient variety of current-voltage combinations are used on the same piece. In any case, the method is inherently destructive and gives only some volume average.

For a free carrier gas, the resistivity is the reciprocal of the product of the carrier charge density times the charge-to-mass ratio of the charge carrier times the mean time between collisions for each carrier. For reasonably isotropic semiconductors, like Si, this product is still a useful guide to interpreting resistivity. Note that in high quality isotropic semiconductor crystals, the principal source of collisions for the electrons is the donor sites from whence they came and the resistivity is a poor indicator

It may well be a useful on-line method for characterizing the bulk resistivity of semiconductor boules being pulled from the melt during space manufacture.

3. Hall Effect

Samples of special geometry are usually cut from the semiconductor crystal to be characterized and so the low frequency Hall effect is destructive and not suited for a central role in the observation of uniformity in carrier concentration. This is unfortunate because the Hall coefficient R_H, directly measured as the ratio of the transverse electric field generated by a steady current flowing perpendicular to a steady magnetic field B to the product of the current and the strength of B, has, for free carriers, the intriguingly simple intrepretation of being the reciprocal of the carrier concentration. As such, the ratio of the measured values of R_H and bulk ρ gives the average carrier mobility over the volume sampled. This mobility of the principal carriers is limited by thermal lattice scattering at high temperatures (the intrinsic region) and by impurity scattering at sufficiently low temperatures to be in the extrinsic region. Characterization by low frequency Hall mobility after growth may well be of some use in the space processing program as an indicator of average quality of the crystals that

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have been grown, but alternate means will be needed to characterize the uniformity of the carrier mobility nondestructively.

4. Gunn Effect

Nonlinearity of the electrical characteristics of a particular semiconductor with respect to the applied fields may be of crucial interest to the intended application. The negative differential permittivity, first reported by J. G. Gunn for GaAs, in the I.B.M. J. Res. Dev. 8 1964, is included in this review as an example of a nonlinearity in a semiconductor response which has rather wide commercial application and depends critically on having a high degree of uniformity over the volume of semiconductor being used in the device.

The Gunn effect permits net amplification of a small electric signal superposed on the bias field whose strength is sufficient to bias the semiconductor into the negative permittivity region, the attainable gain being proportional to the slope at the operating point. The physical explanation of the negative conductance or Gunn instability involves scattering electrons out of the high-mobility (000) conduction band minimum into the low-mobility (100) minima. (ACK67) It is, therefore, not surprising that more recent reports indicate that nonuniform concentration of dopant atoms reduces the extent of the Gunn effect and, thereby, reduces the gain available in amplifier applications. (GL071)

5. Skin Effect Anomaly

The classical skin effect relates the skin depth, δ, to the square root of the ratio of resistivity to the frequency of probing radiation assuming Ohm's law applies on a microscopic scale. However, when the electron mean-free path becomes larger than the classical skin depth, the induced currents extend beyond the field producing them and the skin depth becomes anomalously large, essentially equal to the mean-free path.

In principle, a semiconductor of sufficiently high quality might reach the range of anomalous skin depth at radio frequency, but in practice today, it takes very short microwaves or infrared to do so.

B. Microwave Frequency Methods - MW

Microwave applications form a reasonable portion of the high-quality semiconductor market. As the quality of the semiconductors improve, the microwave performance will also improve and the market expand. Uniformity of dopant concentration and reduction of strains are known to be desired improvements.

In addition to being able to measure directly the specific electrical parameter(s) needed in a microwave application, microwave methods offer the potential of noncontacting scanning for the standard electrical parameters as listed above. Reports in the literature usually show microwave measurements being made on small chips of semiconductor suspended inside waveguide or, for enhanced sensitivity, suspended inside a resonant cavity. However, the waveguide or cavity loading by the semiconductor surface can be accomplished through an appropriate coupling iris so that scanning of the surface is accomplished by simply sliding the surface past the iris, without conducting contact to the microwave circuit. At 35 GHz or 8 mm, irises as small as 1 mm diameter should give useful sensitivity, i.e. uniformity to a few percent at typical resistivity values. (CAS75)

1. Surface Resistance

Noncontacting sampling of the surface resistance of a flat semiconductor surface is readily accomplished at 35 GHz through an iris, typically a few mm across. The analysis of the microwave circuit losses is straightforward as long as the classical skin depth applies. The effective mean resistivity is then determined for the volume formed by the sampled areas of the semiconductor within one δ of the surface. (CAS75). This technique applies equally well to the whole range of semiconductors depending only on the smoothness of the surface for reproducible coupling to the semiconductor.

2. Microwave Hall Effect

In principle, the microwave Hall effect can be used to scan the surface of a high-quality semiconductor in a noncontacting manner, by being the only source of coupling between two degenerate modes of a microwave guide (or cavity). In practice, it is very difficult to achieve because of the high degree of symmetry required in the coupling to the semiconductor surface. Furthermore, the sensitivity is expected to be less than for the surface resistance scanning. Therefore, it is recommended that some other effect such as spin resonance be used to characterize the carrier density. (CAS 75)

3. Microwave Faraday Rotation in Reflection

It is possible that a microwave antenna pattern reflected from a smooth semiconductor surface can be made to contain the Hall mobility information. The averaging would then be over an area measuring at least several wavelengths.

No publications were found.

4. Microwave High-field Permittivity

This special nonlinear response of semiconductors like GaAs was disussed under Low Frequency Methods. When the high (biasing) electric field is at low frequency, space charge accumulates and masks the characteristics of the material host. The use of microwave frequency bias fields permits characterization of the permittivity without effects from space charge buildup. For example, Glover reports avoiding space charge effects by using a 35 GHz magnetron to generate the 12+ kV/cm electric field along a GaAs post suspended across a waveguide. (GL071) As mentioned above, Glover did find an undesirable decrease in the slope in the negative region due to nonuniformity of dopant concentration.

5. Electron Spin Resonance

High quality semiconductors yield electron spin resonance (ESR) signals with reasonable signal-to-noise from a volume as small as a few hundreths of a cubic millimeter even at room temperature. The ESR signal reveals the carrier spin lifetime from the width of the resonance and the carrier concentration from the area under the ESR absorption. The scanning of a semiconductor surface for ESR signals could be done in a noncontacting fashion by coupling through an iris in the cavity wall, just as for surface resistance, plus the magnetic field for ESR, of course. When observed at low temperatures, ESR can yield considerable details about the impurity sites as well. (WAG73)

6. Cyclotron Resonance

Low temperatures are required to get the carrier collision time to be long enough to give resolved cyclotron resonance at microwave frequencies, i.e. to get $2\pi f T > 1$. The resolved cyclotron resonance signals give the collision time for each type of carrier directly. For any sample with $2\pi f T > 1$, the cyclotron resonance signals are much stronger than the ESR signals and can be derived from nondestructive noncontacting coupling in the same way.

C. Infrared and Optical Frequency Methods - IR and OP

The infrared and optical regions span most of the energy level spacings of interest in characterizing electrically any particular semiconductor. The energy spacings include the band gap and the trap depths to impurity levels. The variety of techniques used to observe them by infrared and/or optical methods is extensive. The volume of the published literature citing feasibility and the theoretical models used to interpret the measurements on individual samples is staggering. In this study, we attempted to find published descriptions of the kind of scanning techniques that could be so effective in identifying nonuniformities in the electrical characteristics of high-quality semiconductors to be grown in extended space flights, and we found none. So in this section, we cite:

1. Representative techniques, which have been recently improved, for obtaining one or more of the electrical parameters from individually mounted samples.

2. Several reviews published recently covering a considerable variety.

It seems to us that to adapt an optical technique successful for measuring a parameter, say, the carrier lifetime with respect to a certain type of deep trap, on individually mounted samples into an effective procedure in which the semiconductor is scanned by the infrared or optical frequency beam can surely be done, given reasonable specification of the conditions during the space flight. To establish an example of the first step in this kind of adaptation, we recently chose the task of surveying the photoluminescence (PL) of high-quality GaAs crystal in order to determine an electrical parameter such as the donor concentration without using contacts. We reported a scan technique successful in mapping the donor concentration in GaAs to a reproducibility of better than 20% using run times of some 20 minutes per spot and a spot size of 0.5 mm diameter. (CAS75).

BIBLIOGRAPHY - As Separate Appendix

References to published work representative of the above techniques of electrical characterization of semiconductors are listed in a bibliography under a separate cover.

IV. SUMMARY COMMENTS

This search for published descriptions of successful nondestructive techniques for electrical characterization semiconductor crystals drew a blank. However, advanced optical scanning methods of control and of electrical characterization must surely be successfully operating at the hands of semiconductor-device manufacturers, in view of the very recent successes discussed in the trade journals involving improved uniformity and reduced scale down to a few microns in lateral dimensions and tens of nanometers in depth.

Clearly there are several infrared and optical techniques discussed in this review, whose potential in-flight use is definitely possible at moderate power and weight conditions and whose expected capability of real time monitoring of one or more pertinent electrical characteristics could permit active control of the semiconductor growth during space flight. The feasibility of the specific adaptations required for use in space processing depends on the numerical values of the uniformity - scale and percentage - needed for the particular semiconductor involved. Given the recent push by semiconductor people toward reliance on ion implantation in preference to diffusion techniques for better control of carrier density, junction thicknesses and the like, the impact of NASA's space processing of semiconductor crystals could well be large but will be essentially in competition with the improvements being wrought by ion implantation methods. Techniques for nondestructive scanning to determine the uniformity of several of the semiconductor's pertinent electrical characteristics do appear to be at hand and ready for adaptation to particular space flight needs.