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STUDY OF MATERIALS FOR SPACE PROCESSING

February 1975

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FOREWORD

The present report, No. PC-NAS-002 dated February, 1975 of Paine College Augusta, Georgia is an Annual Report for Grant No. NSG-8002, entitled, "Study of Materials for Space Processing." This report covers the period from January 15, 1974 through January 14, 1975.

The work reported herein was performed under the technical direction of Mr. Tommy C. Bannister of Space Sciences Laboratory, George C. Marshall Space Flight Center, Huntsville, Alabama.

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ABSTRACT

During this period major emphasis has been placed on the development of a handbook of candidate materials feasible for growth in space in future NASA space missions. Materials have been selected from the point of view of device applications and their immediate and near future commercial use. Experimental arrangements have also been made for electrical characterization of single crystals using electrical resistivity and Hall effect measurements. The experimental set-up has been tested with some standard samples.

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INTRODUCTION

The concept of manufacturing in space was first discussed in 1968 (ref. 1) at the Marshall Space Flight Center in Huntsville, Alabama. It was emphasized that man's demonstrated ability to perform productive tasks in space, in order to realize a potential which will have a more direct and immediate impact on the industrial, scientific and economic strength of our society must be exploited. Later, in 1969 (ref. 2), another conference on space processing and manufacturing was held and many scientists joined together to propose possible and promising areas where growth in space in a near zero-gravity environment will be beneficial to mankind. The results of the Skylab experiments (ref. 3) have strikingly verified the utility of space for research purposes. The high proportions of interesting results indicate that space environment will be a fertile field for new discoveries in the area of material science.

The eventual processing of materials in space is likely to become the major economic use for space technology. It holds great potential for technologically benefiting the preparation under micro-gravity conditions of numerous products through imporvements in size, shape, purity or perfection, and the resulting properties. These are expected to markedly benefit man's material well-being.

Considerable efforts during the past seven years have given numerous technologically sound ideas for material science and manufacturing in space. The scarcity of space flights in the decade of 70's prior to availability of the Space Shuttle have made this project timely in providing information on which to base research and development programs in the field of crystal growth.

The report on this project is divided into three parts.

1) The first part deals with the experimental set-up with a view to characterize single crystals of semiconductors and metals by electrical and magnetic measurements. Such measurements will elucidate the role of gravity on the growth of single crystals.

11) The second part of the project deals with the identification of materials suitable for growth and improvement in the low-gravity environment of future flight missions of National Areonautics and Space Administration (NASA). To alleviate the problem of data collection and comparison for scientists designing flight experiments and to provide a basic treatise on the use of such data, a handbook of space-processing materials has been compiled.

In selecting the materials for space processing, emphasis has been placed on those references where single crystal growth is involved and the materials are useful for some kind of device purpose. Data has also been obtained from the principal investigators of the Skylab experiments, and is included herein.

111) In part III data on different materials has been consolidated in a tabular form according to each type of device.

Major efforts in this reporting period were devoted to the development of the handbook of space processing materials.

PART I

Experimental Characterization of Single Crystals

The concept of material characterization plays an important role when we deal with single crystals. The chemical purity or perfection of single crystal semiconductors is only one consideration. A complete evaluation or characterization of a material includes structural properties such as crystallographic defects and physical properties such as mobility and lifetime. Electrical properties are specifically important because these are final criteria by which the quality of crystals are judged.

The concept of material characterization has been clarified recently by a committee of the Materials Advisory Board of the National Research Council (ref. 4) which defines that characterization describes those features of composition and structure (including defects) of a material that is significant for a particular preparation, study of properties, or use, and suffice for the reproduction of the material.

Electrical measurements play a significant role in the evaluation of single crystals of high purity. These are direct measurements of chemical and physical imperfections in the host crystal. Each type of electrical measurement provides a different type of information about a crystal. The Hall coefficient and electrical resistivity yield the mobility and net majority carrier concentration. The sign of the Hall coefficient gives the carrier type, positive for p-type and negative for the n-type.

For measurement of resistivity, the following three methods have been set up.

1) Two-point probe method.

2) Four-point probe method.

3) Vander pauw method.

1) Two-Point Probe Method

Experimental arrangements have been made for measurement of resistivity by the two-point probe method (ref. 5). Basically the procedure involves making ohmic contacts to the end of the sample, passing a known current through the sample and then measuring the voltage drop across the two probes applied to the surface. The resistivity is then calculated:

$$\rho = \frac{V}{I} \cdot \frac{A}{L} \text{ ohm. Cm.}$$

where A = Cross-sectional area normal to the current

L = Distance between the probes

I = Constant current

V = Potential drop measured across two probes

The current through the sample is measured by measuring the potential drop across a standard 1 ohm resistor in series with the sample, and the voltage drop measured with a Keithley model 610C electrometer. The set-up can be used to determine resistivity of semiconductor and metal samples cut in the shape of a rectangle.

The set-up has been tested with samples of InSb and Bismuth single crystals.

2) Four-Point Probe Method

The four-point probe techniques developed by Valdes (ref 6) has been set up to measure the resistivity of samples in the form of flat discs. According to Valdes, the resistivity, ρ, is given by,

$$\rho = 2\pi a. \frac{V}{I} \text{ ohm. cm.}$$

where the distance, a, between each of the four equidistant probes is usually up to about 0.13 cm., V is the potential measured across the inside probes and I is the current passing through the two outer probes.

The set-up has been tested using samples of known resistivity and after applying the correction factors as proposed by Valdes.

3) **Vander-Pauw Method**

Experimental arrangements have been made for the measurement of resistivity and Hall effect (dc-dc) using the method developed by Vander Pauw (ref. 7). The Vander Pauw method requires plane paralled samples of arbitrary shape with four or more ohmic contacts on the surface. A current is passed between the two adjacent contacts while the potential difference is measured between the other two. By cyclic permutation, two independent pseudo-resistances, R_1 and R_2, are obtained as voltage and current ratios. It has been shown by Vander Pauw that,

$$\rho = \left(\frac{\pi d}{2 \ln 2}\right)(R_1 + R_2)\ f\ \frac{R_1}{R_2}$$

where ρ is the resistivity and 'd' is the platelet thickness.

The function of $f\left(\frac{R_1}{R_2}\right)$ is given by Vander Pauw and depends only on the ratio $\left(\frac{R_1}{R_2}\right)$.

The Hall coefficient R_H can be determined by passing a current in the non-adjacent contacts. The change in voltage can be measured across the other contacts when a magnetic field is applied perpendicular to the sample. The Hall coefficient R_H is given by:

$$R_H = \frac{d}{B} R_3$$

where B is the magnetic induction, R_3 is the change in resistance R_3 with the magnetic field and 'd' is the thickness of the sample.

Also $R_H = \frac{1}{ne}$ which gives the value of the carrier concentration, 'n'.

The mobility μ_H can be calculated from the expression,

$$\mu_H = \frac{R_H}{\rho}$$

The homogeniety of the samples can be measured by measuring the resistivity and Hall coefficient, using more than four contacts on the sample. Ohmic contacts on the order of six or eight are very useful in determining the electrical homogeniety of the samples.

Recently, the Vander Pauw method has been used by the Westbrook (ref 8) to identify the effects of semiconductor inhomogenieties on carrier mobilities.

At present, the experimental set-up has been made for measurements at room temperature only. This set-up can also be easily adapted for low temperature work.

Part II

II. 1. Compilation of Data for Candidate Materials for Space Processing

To fully utilize the low gravity environment for material processing, it is useful to make a survey of the possible candidate materials feasible for growth during the future space flights sponsored by NASA. To accomplish this task, a survey was made of the available literature in the area of crystal growth in the open scientific journals and other NASA and federal reports. Special emphasis has been placed on those materials which can be improved in the zero-gravity environment and have a large impact for scientific and industrial use.

Articles published in the area of crystal growth and related fields have been obtained by scanning the two major abstracting journals, namely Physics Abstracts and Solid State Science Abstracts. Also, important journals in the area of Solid State Physics, Applied Physics, Material Science, Crystal Growth and Solid State Electronics have been reviewed for each month. Data published prior to the last five years has been obtained through important review articles and other books. Data on the previous flight experiments in the Skylab mission has been obtained from the Principal Investigators of the experiments and through the proceedings of the Skylab conference at NASA.

II. 2 Physical Phenomena Related to Crystal Growth in the 0-gravity

This study is aimed towards the identification of the most likely technological area of crystal growth to be improved by production in space.

Crystal growth of solid state materials from the melt, the solution, and the vapor-phase is an art of many years. With the advent of semiconductors in the late forties, crystal growth techniques have advanced rapidly and considerable progress has also been made in understanding crystal growth processes. The properties of electronic materials are strongly dependent on structural perfection. For example, grain boundaries act as carrier recombination centers and mobility scattering centers. Also, the boundary now acts as an insulating layer, and measured properties of polycrystalline material may be more indicative of the properties of the grain boundaries than of the true properties of individual crystal growth.

Chu (ref 9) has studied the phenomena related to crystal growth in space. Nearly all crystal growth processes involve both a solid and a liquid component. Since internal bonding forces in solids are much greater than 1-g forces, and the familiar properties of the liquids are the result of the interaction of intermolecular forces and the gravitational force. If the gravitational force disappears, the behavior of fluids will be determined by the molecular forces alone. Thus, the near-zero gravity conditions will have a significant influence on the fluid behavior which may affect the crystal growth process.

Melt growth is the most important technique for the production of large crystals of electronic materials. In the Czochralski technique, with the melt contained in a crucible, force convection is necessary to overcome the random thermal fluctuations due to natural convection and to minimize the impurity inhomogeneity in the melt due to segregation. The greatly reduced free convection in the space environment will mean that forced convection will be of still smaller magnitude. In the float zone and the crucibleless technique, the surface tension of the melt and the levitating electromagnetic field overcome the gravitational force to support the molten zone. The crucibleless technique will therefore most directly demonstrate the unique effects of the greatly reduced gravity in space environment.

II. 3. Format of the Handbook

In the present study, the following categories of materials have been considered:

- a) Electro-optic materials - lasers, electro-optic switching memory devices, and electroluminescent devices
- b) Materials for microwave devices - IMPATT, varacter diodes, detectors, field effect transistors, mixers, etc.
- c) Acousto-optic materials
- d) Materials for magnetic memory devices - non-cubic garnets
- e) Materials for radiation detectors
- f) Materials for energy conversion devices

In each category, different materials in use at the present time are being considered keeping in mind the temperature requirements of the furnace in the space laboratory (1500°C at the present time). The requirements of the material for each category has been given. Based on the design criteria, recommendations are given for the two best materials in each category to be considered for growth in zero-gravity environment.

The final data has been given in a tabular form in part III of the report. Relevant references are included at appropriate places. A detailed list of bibliography of references collected on different growth techniques and devices is included at the end of the report in appendix I. Since the number of references collected during the reporting period is extremely large, only the references directly dealing with different device materials have been included herein.

II. 3. a) Materials for Electro-optic Devices

Electro-optic materials are needed for optoelectronic devices which convert electrical energy into optical radiation or vice versa, and for those which detect optical signals through electronic processes. One of the most important of these is the semiconductor laser. Others include electroluminescent devices, photovoltaic devices and photodetectors. The photovoltaic devices will be dealt in section 'f' seperately because of their recent importance. Also photodetectors will be dealt separately in section 'e'.

I) Laser Materials

Semiconductor lasers are similar to other lasers (such as the conventional solid state ruby laser and the He - Ne laser) in that the emitted radiation has spatial and temporal coherence. This means that the laser radiation is highly monochromatic and that it produces a highly directional beam of light. However in semi-conducting lasers, the quantum transition is associated with the band properties of the material. The spatial and spectral characterstics of semiconductor lasers are strongly influenced by the properties of the junction medium such as doping and band tailing.

The list of semiconductor materials which have exhibited laser action has continued to grow in the last ten years. Table I shows a list as complied by Nathan (ref. 10) for materials which have lased, together with the photon energy of oscillation, the corresponding wavelength, and the method of excitation. GaAs was the first material to lase. As seen from table I, the wavelength extends from the ultraviolet to mid - infrared.

TABLE I (ref. 10)

LASER MATERIALS

Material	Photon Energy (eV)	Wavelength (microns)	Method of Excitation
ZnS	3.82	0.32	electron beam
ZnO	3.30	0.37	electron beam
CdS	2.50	0.49	electron beam, optical
GaSe	2.09	0.59	electron beam
CdS_xSe_{1-x}	1,80-2.50	0.49-0.69	electron beam
CdSe	1.82	0.68	electron beam
CdTe	1.58	0.78	electron beam
$Ga(As_xP_{1-x})$	1,41-1-95	0.88-0.63	p-n junction
GaAs	1.47	0.84	p-n junction, electron beam, optical, avalanche
InP	1.37	0.90	p-n junction
$In_xGa_{1-x}As$	1.5	0.82	p-n junction
GaSb	0.82	1.5	p-n junction, electron beam
InP_xAs_{1-x}	0.77	3.1	p-n junction, electron beam, optical
InSb	0.23	5.2	p-n junction, electron beam, optical
Te	0.34	3.64	electron beam
PbS	0.29	4.26	p-n junction, electron beam
PbTe	0.19	6.5	p-n junction, electron beam, optical

TABLE I (continued)

Material	Photon Energy (eV)	Wavelength (microns)	Method of Excitation
PbSe	0.145	8.5	p-n junction, electron beam
$Hg_xCd_{1-x}Te$	0.30-0.33	3.7-4.1	optical
$Pb_xSn_{1-x}Te$	0.09-0.19	6.5-13.5	optical

Recently a new intermediate gain laser material has been reported by Watts and Holten (ref 11). Two such intermediate gain Nd laser materials are $CaLa_4 (SiO_4)_3 O$:Nd and $(Y_3Al_{1-x}Ga_x)_5 O_{12}$: Nd. Excellent optical quality spectroscopic crystals have been prepared by the Czochralski growth technique. These materials can be improved by growing in a low-gravity environment.

II) Electroluminescent Materials

A new and promising technology based on electroluminescence is now being developed. Electroluminescence is the direct conversion of electrical energy into radiation without the utilization of an intermediate form of energy such as heat. The emission characteristics depend upon the chemical composition of the host crystal and the incorporation of small amounts of certain impurities.

Electroluminescence (visible and infrared) associated with the application of a small d.c voltage to a p-n junction or a light emitting diode (LED) is of great importance.

Design criteria for light emitting diodes have been discussed by Duke et.al (ref. 12). The important points are as follows:

1. The light emission must occur in the visible frequency range from red (λ = 6800 Å) to the blue (λ = 4500Å)

2. It must be possible to make a p-n junction in the base semi-conductor material.

3. The conversion of electrical energy to the visible light at this junction must be relatively efficient. That is, the LED should have a luminous efficiency of 0·1 - 0·2 lumens/w or a brightness of 50 - 100 ft-lamberts/A/cm^2 or higher.

Due to the difficulty of satisfying all three criteria simultaneously and inexpensively the development of semi-conductor lamps and visible semiconductor lasers has been delayed.

Applications (Light Emitting Diodes)

The most glamorous potential application of visible light emitting diodes is in the falt screen color TV displays, a development which appears to lie in the future. A more prosaic but immediate application is the use of visible LED's as simple indicator lamps. Indeed LED's which emit in the red, green or yellow are now available commercially with most emphasis being placed on $GaAs_{1-x}P_x$, Si- dopod GaAs coated with a green producing phosphor, and SiC. Surprisingly the most efficient red and green emitter, GaP, is not on the list of commercially obtained diodes. This relative lack of attention to GaP has been due to number of factors, including the lack of large area GaP substrates (prior to crystal pulling), the relative ease of growth of $GaAs_{1-x}P_x$ and GaAs, and the fact that efficiency of red emitting GaP LED's is maximized at relatively low currents. According to Casey Jr. et.al (ref. 13), a very large market (tens of million) exists for LED indicator lamps for telephones where bright LED's low currents (1-10ma) are required.

Thus it appears that GaP has a large potential for high efficiency low current LED in the commercial market. Growth in space to produce large area substrates will be a potential improvement in the technology.

Properties of Gallium Phosphide Which Makes It Well Suited For Electro-Optic Modulator

1. The transeverse electro-optic effect is operable in this material, which makes it possible to increase the path length of the modulated radiation without increasing the applied voltage.
2. GaP is a cubic crystal and therefore does not introduce critical optical alignment porblems associated with birefringent crystals, such as ADP (ammoniam dihydrogen phosphate), KDP (potassium dihydrogen phospahte).
3. GaP is not ferroelectric and so does not require critical temperature control as does potassium tantalate niobate (KTN).
4. GaP is mechanically a very strong crystal and is not affected by normal atmospheric conditions or temperature varitions.
5. Finally, it is transparent to much of the visible spectrum of radiation and therefore serves as an extension of GaAs which has been sucessfully used for electro-optic modulation of infra-red radiation.

DATA ON IMPORTANT ELECTRO-OPTIC MATERIALS

Bismuth Titanate $Bi_4Ti_3O_{12}$ (ref. 14)

Growth Method: Epitaxial films by r.f. sputtering from ceramic targets. (010 orientation)

Growth Temperature: 725° C

Substrate: $MgAl_2O_4$ (110), sapphire Al_2O_3, and rutile (TiO_2)

Film Thickness: 10 µm

Applications: Electro-optical switching, optical display and memory application.

Comment: Cracking and peeling of films due to mis-match in the thermal expansion coefficients of the film and substrate.

$Ba_x Sr_{1-x}Nb_2 O_6$ and $Ba_2 Na Nb_5 O_{15}$ (ref. 15)

Growth method: Czochralski

Melting temperature: $Ba_x Sr_{1-x} Nb_2 O_6$ - 1500° C

$Ba_2Na Nb_5 O_{15}$ - 1440° C

Applications: Low voltage deflectors, non-linear optics (Harmonic generation)

Comments: Heterogeneities of refractive index (Striae) are major reasons for limiting the optical quality. Super-cooling phenomena is the origin of these variations in impurity concentrations. By avoiding thermal fluctuations near the growth front and by using raw materials of higher purity, it is possible to grow better crystals. These have great potential for improvement in 0-gravity.

Zinc Oxide ZnO (ref. 16)

Growth method: Epitaxial films by chemical vapor deposition (CVD) $(11\bar{2}4)$

Growth temperature: 700 - 900° C

Substrate: Sapphire $Al_2 O_3$ (0001)

Film thickness: 2 μm.

Applications: Electro-optic and acousto-optic interation devices

Comments: Major problem encountered is the inability to produce proper orientation. One single material can be used for two different devices. Has potential for improvement in low gravity environment.

Lithium Iodate α- $LiIO_3$ (ref 17)

Growth Method: Solution method by slow evaporation process at constant temperature.

Growth Temperature: Between 50-80°C

Applications: Second harmonic generation. Has large non-linear coefficient comparible to that of $LiNbO_3$. It is less susceptible to optical damage and large clear crystals can be grown.

Comments: Striae were produced causing severe distortion of laser beam. In low-gravity environment, large optically homogeneous crystals can be grown.

Lithium Niobate $LiNbO_3$ (ref 18, 19, 20, 21)

Growth method: Czochralski (ref 17 & 19), epitaxial growth by melting (EGM), (ref 18)

Growth temperature: 1250°C (ref 18)

Substrate: $LiTaO_3$ (ref 18)

Applications: Light modulator, optical communication system or optical data processing; optical wave guide, second harmonic generation (SHG)

Comments: Under very special growth conditions, fine optical quality crystals obtained in laboratory are susceptible to optical damage, although this has been overcome to a large extent (ref 17). This material has a large potential for commercial use and can be improved in 0-gravity growth.

GaAs - Gallium Arsenide (ref 22,23,24)

Growth method: Czochralski, horizontal Bridgman, vertical gradient freeze

Growth temperature: 1240°C

Form of crystal: Bulk

Application: Substrate for LED and other epitaxial films

Comments: Because of the high vapor pressure of arsenic, deviations from the stoichiometric melt composition are almost inevitable, which in turn affect the crystallinity. To obtain good quality epitaxial films, it is essential to have a substrate which is defect free. Growth in a low-gravity environment will be a significant improvement in the crystal quality.

GaAs - Gallium Arsenide (films) (ref. 23,25,26,27,28,29)

Growth method: Liquid-phase epitaxy, vapor-phase epitaxy

Growth temperature: 850°C

Substrate: doped GaAs

Applications: Semiconducting lasers, light emitting diodes, high temperature transistors and field-effect transistors, solar cells

Comments: Liquid-phase growth at low temperature imposes difficult problems with thickness uniformity and surface smoothness. In solution growth, there is a strong tendency to form a relatively small number of nucleation sites on the substrate surface. Low gravity environment may solve the problem. In chemical-vapor deposition, the possible toxicity may be a harmful cause. This material has advantages over Silicon for the energy conversion devices. GaAs solar cells are superior to Si cells in most irradiation conditions.

GaP - Gallium Phosphide (ref 13,25,30)

Growth method: Vapor growth, floating zone method, solution method

Growth temperature: 1060°C (much below its mp - 1460°C)

Substrate: GaAs or Sapphire

Applications: Presently it is used for Schottky barrier diodes. Has a potential use as an electro-optic modulator of visible radiation, LED, secondary-emission dynodes

Comments: The utility of the crystal is limited because of problems related to slight crystalline strain. Good area is limited to 10 sq. mm. Areas as large as 1 sq -cm. without crystallographic defects is desired. This material has a large potential for improvement in low-gravity crystal growth. The preparation of acceptable high purity GaP may depend on development of low temperature solution methods and the adaptation of vapor or chemical methods to the growth of sizable crystals or single crystal films.

Alloys of 111-V Compounds - $GaAs_{1-x}P_x$ (ref 13,25,31,32)

Growth method: Vapor growth

Growth temperature: 400-900°C

Substrate: Ge, GaAs

Applications: Electroluminescent diodes, room temperature injection laser, high temperature rectifier, high temperature transistors and photocathodes

Comments: Electron concentration less than $1 \times 10^{15}/cm^3$ is needed. Microplasma free p-n junction as large as 0.175 in is a major constraint. Very difficult to get defect-free p-n junction of the above dimension. This material has a very great potential to be used commercially in the near future. Better homogeneous films can be obtained in a low-gravity environment.

YAG Single Crystals (ref 33)

Growth method: Czochralski

Growth temperature: 1900°C

Doping: Nd-doped

Applications: Optical, lasers and jewelry

Comments: Growth interface providing the best laser results has often found to be a faceted interface which showed (211) facets in the core and (110) facets on the outer region, when growth directions were the (001) and (111) axes. This material is almost certain to be used commercially in the near future, and has a great potential for improvement in a low-gravity environment.

YVO_4 - Yittrium Vanadate (ref 34, 35, 36)

Growth method: Floating zone, Czochralski, flux growth

Growth temperature: 1400°C

Applications: Laser, optical, IR windows

Comments: Out of these methods, the flux growth is expensive and uncertain as to the crystal size and quality. The crystal grown by Czochralski technique are usually dark. Crystals grown by modified floating zone method (ref 36) were found to be light yellow and transparent. Annealing at 1500°C in oxygen eliminates the yellow color. Low-gravity environment growth has a large potential for growing bigger and more homogeneous crystals. This material may be used commercially in the near future.

$CaCo_3$ - Calcite (ref 37)

Growth method: Travelling solvent zone method, flux method

Growth temperature: ∿1339°C

Applications: Optical work, polarized light

Comments: One of the main difficulties encountered in the preparation is the dissociation of $CaCO_3$ with rise in temperature. Also, another difficulty encountered in growth is the formation of gas bubbles in the liquid zone which become partly confined in the grown crystal. Although gas bubbles may be more of a problem because of reduced convection, the simplified floating zone is an added advantage.

$K_{0.5}Na_{0.5}NbO_3$ - Potassium-sodium Niobate (ref 38,39)

Growth method: From molten solution

Growth temperature: ∿1100°C

Applications: Communication equipment, computers, infra-red sensors, miniaturization of electronic circuits, lasers, radars amd sonar uses.

Comments: Many electronic ceramics are produced in polycrystalline form. Electronic properties of oxidic materials are very sensitive to purity, crystal structure and crystalline perfection. Availability of single crystals could result in increased efficiency. The zero-gravity environment has a great potential for growing larger, and defect-free crystals.

II. 3. b) Material for Microwave Devices

In this section, semiconducting materials which are needed commercially for the fabrication of microwave devices are discussed. Most of the microwave devices are fabricated within the epitaxial layer. High quality devices impose the following requirements:

1. Uniform distribution of dopant in the plane of junction with very little variations of the doping level perpendicular to the junction.
2. Precise thickness control and junction planarity over large area. (over an inch in diameter)
3. Smooth surface morphology.

The above requirements impose strong conditions for the crystal quality. Shaw (ref 23) and Grove (ref 40) have discussed in detail the semiconductor materials needed for microwave devices. Materials for the following devices will be discussed.

i) Transferred electron devices

ii) Avalanche diodes (IMPATT)

iii) Varacter diodes

iv) Field effect transistors

v) Power rectifiers

I) Transferred Electron Devices (TED)

These microwave devices make use of a negative conductance phenomena which results from the transfer of carriers from a low energy, high mobility conductor valley to higher subsidiary valleys with lower mobilities under the influence of an applied electric field.

They include Gunn Effect Devices or transferred electron oscillators (TEO) and transferred electron amplifiers (TEA).

Requirements of Materials (ref. 41)

- a) A relatively low lattice temperature must prevail so that most of the carriers are in the lower conduction valley in the absence of an applied electric field.
- b) Carriers in this valley should have low effective mass which correspond to a low density of states and high mobility. The opposite should be true of carriers in a subsidiary valley.
- c) The energy separation between the conduction valleys must be less than the energy gap separating the valence and conduction bands so that a negative conductance occurs prior to avalanche breakdown as the applied fields increase.

Materials in Use

GaAs, InP, CdTe, ZnSe, $Ga_xIn_{1-x}Sb$

The material parameters which must be carefully controlled for these devices are the epitaxial layer thickness and the carrier density. High frequency operation requires thinner layers with greater carrier densities. In general, TE devices place more severe demands on the quality of the epitaxial layers. GaAs remains the only material which has made the transition from the laboratory to a commercially available device.

II) Avalanche Diodes (IMPATT)

Avalanche diodes generate microwave oscillations from the negative conductance which results from two factors:

1) Time delay between the applied voltage and the resulting current due to avalanche at a junction
2) The transit time delay from travel of carriers through the diode. IMPATT diodes have been formed in GaAs, Si, and Ge.

However, from the theoretical point of view, GaAs is superior in most respects.

GaAs IMPATTs have a higher theoretically efficiency (23% as compared with 15% for Si). (ref. 42)

The noise figures for GaAs devices are theoretically lower than Si and it has been demonstrated that GaAs devices can simultaneously produce greater conversion efficiencies and lower noise figures.

Much of the effort to improve IMPATT performance is currently centered around the production of devices with specially tailored doping profiles.

Crystal growth in space environment can be of significance towards the improvement of crystal homogeneity and uniform doping profiles.

III) Varacter Diodes

Varacter diodes exhibit variations in junction capacitance with applied voltages and serve as units of variable reactance for harmonic generation, tuning, switching and mixing. (ref. 43)

Requirements of Material

a) A high carrier mobility to maintain a minimum electrical resistance.
b) A low dielectric constant for minimum capacitance.
c) A large energy gap to minimize saturation current and for potential higher temperature operation.
d) A high thermal conductivity.

An examination of Table II reveals that GaAs is superior to Si in all respects except thermal conductivity. Ge possesses no clear cut advantage over Si and is more difficult to process.

TABLE II (ref 43)

Material	Energy Gap (ev)	RT. Mobility $cm^2/v.$ sec electrons	holes	Thermal conductivity w/cmk	Dielectric constant
Si	1.1	1500	600	1.45	12
Ge	0.67	3900	1900	0.64	16
GaAs	1.4	8500	400	0.46	12
InP	1.3	4600	150	0.65	14

Thus Silicon and GaAs are the dominant varactor materials with the latter being superior, particularly for more demanding applications

IV) Microwave Field Effect Transistors (FET)

In the early 1960s, considerable efforts were directed to the investigation of thin film bipolar transistors by a number of industries. This development has virtually ceased (ref. 44), although field effect transistors (unipolar transistors) on gallium arsenide have been developed to a prototype production stage for high frequency operation.

Material Requirements

a) high mobility
b) high saturation velocity
c) well developed Schottky barrier technology
d) a semi-insulating substrate for an active epitaxial layer

Gallium Arsenide possesses a unique combination of properties which make it a suitable material for microwave FETs.

Advantages to be Expected from Gallium Arsenide Transistors (ref. 45)

1. GaAs by virtue of its high electron mobility and large gap, would be a useful material.
2. Can be used for high power, high temperature and high frequency transistors.
3. In high temperature limits, GaAs is superior to both Ge and Si . High temperature behavior of a transistor depends on the intrinsic carrier concentration of the material. The highest temperature at which a transistor will operate is arbitrarily considered to be the temperature at which the intrinsic carrier concentration would equal that of Ge at 100° C. For Si and GaAs these are 250 and 450° C respectively.
4. The power gain-band width porduct of a transistor is related to the maximum oscillating frequency,

   $$(\text{power gain})^{\frac{1}{2}}\ (\text{band width}) = \text{maximum oscillating frequency}$$

   Thus gallium arsenide has an advantage over Si. (see table III)
5. Gallium arsenide can be obtained with a high resistivity (10^8 ohm cm). Integraged circuit elements could be formed in an epitaxial layer on a semi-insulating substrate and would not need to be isolated by p-n junctions as in the case of Si integrated circuits.

TABLE III (ref. 45)

Some Physical Properties of Ge, Si, and, GaAs

Parameter at 25°C	Ge	Si	GaAs
Energy Gap (eV)	0.72	1.11	1.40
Intrinsic Resistivity (ohm-cm)	46	2.3×10^5	3.7×10^8
Electron Mobility at 5×10^{16} cm^{-3} (cm^2 V^{-1} sec^{-1})	2500	700	6000
Hole mobility at 5×10^{16} cm^{-3} (cm^2 V^{-1} sec^{-1})	1250	270	300
Thermal conductivity (W cm^{-1}°C^{-1})	0.55	1.45	0.44

It is generally agreed that trapping states are the main cause of the poor performance of the transistors. An improvement in gallium arsenide material technology may eventually lead to a viable GaAs transistor. GaAs is better or equal in many respects to Ge or Si.

V) Power Recitifiers

It has been demonstrated (ref. 46) that rectification can occur in GaP at temperatures up to 500° C. The reverse voltage obtained to datc must be improved before a practical rectifier can be commercially made. GaP and SiC are the only materials to date in which useful rectification ratios ($\gtrsim 10^2$) have been obtained in 400° C ambients. For this application, gallium phosphide as compared to silicon carbide possesses a lower forward drop and, assuming that the reverse voltage can be improved, should be the better of the two materials, particularly in view of the usual military requirement for operation over a range of temperatures down to -55° C.

It appears that the most immediate improvements to be made are increasing purity and improving crystal perfection of GaP crystals. Crystal growth in low gravity environment has a large potential for improving the homogeneity of the material.

Data on Promising Materials for Microwave Devices

$In_{1-x}Ga_xP$ (ref. 47, 75)

Growth method: Open tube vapor growth technique.

Growth temperature: 700-800°C

Substrate: GaP wafers

Applications: Electroluminescent diodes, injection laser diodes

Comments: Low electroluminescence efficiencies, perhaps due to crystal strain and compositional inhomogeneity. Have large potential for imporvement in a low-gravity environment.

$Al_xGa_{1-x}As$ (p-type) (ref. 48)

Growth Method: Molecular beam epitaxy, liquid phase epitaxy and vapor phase epitaxy

Growth temperature: 1350°C

Substrate: GaAs

Applications: LED, integrated optics, hetrostructure laser

Comments: The present porblems include, uniformity over the entire growth area; good surface morphology and controlled layer thickness on a routine basis. The constancy of lattice parameters with GaAs makes $Al_xGa_{1-x}As$ alloy system of great interest since the attainment of low-strain large bandgap epitaxial layers are more readily achieved than in a system where grading is required. This alloy system has a large potential for improvement in low-gravity environment and has a great commercial value.

Silicon Si (Bulk) (ref. 49, 50)

Growth method: Czochralski, floating zone

Growth temperature: 1430°C

Applications: Semiconductor devices, IR windows, Avalanche detectors can be used to detect radiation in many low energy nuclear applications in medicines.

Comments: Typical silicon wafer specifications require a wafer diameter of 2-3" with a dislocation density of 1000/cm^2. With the present trend, a larger diameter wafer will be required by the industry during the last half of this decade. The production of large diameter crystals with minimum dislocation density will be potential improvement in a low-gravity environment.

Silicon Si (epitaxial films) (ref. 51, 52, 53)

Growth method: Chemical vapor deposition, implant-epi process (ref. 52)

Growth temperature: 1000-1300°C

Substrate: Graphite, graphite coated with SiC, Sapphire, Silicon Nitride (ref. 52)

Applications: Semiconductor devices, monolithic integrated circuits, solar cells.

Comments: The need for higher device operating frequencies for faster data processing or more efficient communications, demands a continually increasing level of control in progressively thinner layers. Typical epitaxial layer thickness for transistor applications ten years ago were around 10μm, where as now 2-4μm is common. Increasing interest in submicron layers now poses new problems in layer deposition. Growth in a low gravity environment seems to be a great potential for improving the crystalline perfection of such films. The semiconducting properties of thin silicon films will improve as the growth temperature is reduced and the growth rate has been increased.

Silicon Si (Polycrystalline films) (ref. 54, 55, 56)

Growth method: Vacuum deposition (ref. 54), pyrolysis in an epitaxial reactor (ref. 55)

Growth temperature: 1000°C (ref. 54)
650-680°C (ref. 55)

Substrate: Fused silica, silicon, oxidised silicon, silicon nitride coated silicon, and sapphire.

Applications: Diodes and MOS devices, solar energy collectors in the harnessing of solar energy

Comments: The impurities in silicon films can be reduced, however, if proper purification techniques in vacuum are employed. The clean vacuum environment of space may present a good opportunity for obtaining better and thinner films with less contamination.

II-3-C) MATERIALS FOR ACOUSTO-OPTIC DEVICES

Acousto-optic devices are becoming increasingly important in the fields of optical information processing and display largely due to the availability of better transducers and hopefully better acousto-optic materials.

In the beginning, the selection of materials was based primarily on the availability of material and on intuition. Now it is possible (ref. 57) to estimate an approximate acousto-optic figure of merit for a material knowing only its chemical composition and density.

Material Requirements

There are two important points to be considered:

1. high figure of merit
2. low acoustic loss

Although limited loss data is presently available, it was concluded by Pinnow (ref. 57), that high figure of merit and low loss are compatible material properties for applications below approximately 0.5 GH_z. However, as future applications call for higher frequency operation, it appears that a trade-off between low acoustic loss and high figure of merit will be required. Additional information concerning hardness of the materials and its solubility in water is also helpful in imporving the estimated value.

A qualitative conclusion that can be drawn from the work of Pinnow that relatively soft, yet dense oxide materials having cations should also have high acousto-optic figure of merit.

A selected list of the most useful or potentially useful acousto-optic materials is given in table IV, in which figure of merit, acoustic loss and range of optical transmission are listed.

Table IV (ref. 57)

Material	Useful Optical Wavelength µm	Figure of Merit M_2	Acoustic Attenuation at 550 MH_z	Comments
Fused Silica	0.2 - 2.5	1.0	3.0	reference material
Water	0.2 - 0.9	106	500	
GaP	0.2 - 0.9	20.5	1	
$LiNbO_3$	0.5 - 4.5	4.6	.05	optical damage
HIO_3	0.4 - 1.3	55	2.5	water soluble
$PbMoO_4$	0.4 - 5.5	23.7	2.5	

The high acoustic loss in water is typical of all liquids (ref 58) and limits their usefullness to frequencies below approzimately 50 MH_z, where the acoustic loss is less than 10 dB/cm. It is apparent that the search for promising acousto-optic material should be restricted to solids, since their acoustic loss may be orders of magnitude less than those found in liquids.

The guidelines as discussed above indicate that $PbMoO_4$ has a high figure of merit, considerably greater than $LiNbO_3$, though somewhat less than α-HIO_3.

The tetrogonal modification of tellurium dioxide, para-tellurite, α-TeO_2, has elastic and optical properties making it particularly attractive for acousto-optic devices. According to Kolb, et. al. (ref 59), the velocity of shear waves in (110) direction is quite low and the index of refraction is high, for example, leading to an acousto-optic figure of merit, M_2, for the (110) shear mode approximately 21 times better than M_2 for $PbMoO_4$.

$PbMoO_4$ (Lead Molybdate) (ref. 57,78)

Growth Method: Czochralski
(rf. induction heating, pulled at about ¼ in. per hour)

Growth temperature: 1060°C

Applications: Acousto-optical devices

Comments: $PbMoO_4$ forms tetragonal crystals and is therefore optically uniaxial and do not exhibit optical activity. It has high acousto-optic figure of merit, low acoustic and optical loss, favorable mechanical impedence for acoustic matching, the absence of optical damage effects such a has been observed in $LiNbO_3$ and easy growth. This has a large commercial importance.

α-TeO_2 - Paratellurite (ref. 59)

Growth method: Hydrothermal crystallization

Growth temperature: 250-385°C

Seed material: Czochralski grown single crystals of α-TeO_2

Applications: Lately, high efficient acousto-optic light deflectors using the interaction of circularly polarized light and the optical activity of TeO_2 have been made. TeO_2 has an acousto-optic figure of merit approximately 21 times that of lead molybdate, $PbMoO_4$, one of the best acousto-optic materials known at present.

Comments: Hydrothermal method is very promising for producing better crystals. This material has a large potential for future commercial use.

II-3-d) MATERIAL FOR MAGNETIC MEMORY DEVICES

In 1967, Boebeck (ref. 60) presented a new memory and logic device using magnetic single crystal materials. These devices use cylindrical magnetic domains (called bubbles) in thin plates of transparent magnetic single crystals.

Material Requirements

The following characteristic properties of bubble domain materials have been given by Challeton, et. al (ref. 61).

i) The domain exists in a plate of magnetic material of uniform thickness.
ii) The magnetization in the plate is constrained to lie normal to the surface of the sheet by uniaxial anisotropy.
iii) Domain wall width is small compared to domain diameter.
iv) Wall-motion coercivity is sufficiently small so that domain size and shape are independent of coercivity.
v) The Curie or Neel temperature of materials must be above the room temperature.
vi) The magnetic properties of these materials have also to be stable in the room temperature range.

The above requirements restrict the use of the following types of materials: orthoferrites, hexagonal ferrites, FeF_3 and $FeBO_3$, spinel and garnets. The specific materials which seem to have a large promise are: $Sm_{0.55}Tb_{0.45}FeO_3$, Fe_5LiO_8, $Tb_3Fe_5O_{12}$, BiCaVIG, YCaVIG, $Y_{2.5}Gd_{0.5}GaFe_4O_{12}$.

The non-cubic garnets are extremely attractive because of the feasibility of growing thin films by liquid epitaxial growth or by hydrothermal epitaxy.

The initial step in achieving high quality magnetic films for bubble domain memory devices is the preparation of suitable substrates. These require a material perfection which is above average for oxide single crystals, combined with a surface finish free from defects which would interfere with the subsequent growth of the epitaxial film. Gadolinium Gallium Garnet (GGG) has emerged as a prime substrate for bubble domain memory devices. Kieg (ref. 62) has discussed in detail GGG substrate growth and fabrication. Further advances in this area are needed and should be realized in the area of substrate surface finish and overall surface flatness. The current substrate diameter requirements are more indicative of the demand.

Much work remains to elaborate thin films, free of defects and useful for practical devices. Manufacturing in space, under reduced gravity conditions, can help grow better films which can be of extreme value for the industries.

$Sm_{0.55}Tb_{0.45}FeO_3$ - Orthoferrite (ref. 61, 79)

Growth method: Flux method. Grown from $PbO-B_2O_3$ flux

Growth temperature: ~ 1300°C

Application: Magnetic bubble memory devices.

Comments: Flux growth might not be an economic growth method for production. The study of orthoferrites shows that in general the bubble size is too large. In some cases very high mobility of the material may be helpful. Non-cubic garnets are better materials for bubble domain devices.

Fe_5LiO_8 - Lithium Ferrite-spinel (ref. 38, 61)

Growth method: Flux method from $PbO-B_2O_3$ flux

Solution temperature: 1060°C

Final temperature of crystallization: 700°C

Applications: Bubble memory devices

Comments: Difficult to prepare thin platelets. Microgravity growth techniques have the potential for controlling the perfection and uniaxial anisotropy which is the key to the bubble size and bubble movement, and therefore information storage and transfer efficiency. Growing of platelets can eliminate unnecessary cutting and polishing operations which are liable to introduce imperfections.

BiCaVIG and YCaVIG - Garnets (ref. 61)

Growth method: Flux method from PbO flux

Solution temperature: 1200°C

Final temperature of crystallization: 1020°C

Applications: Computer memories, display devices.

Comments: Same as spinels

$Gd_xY_{3-x}Ga_yFe_{5-y}O_{12}$ - Garnets (ref. 61)

Growth method: Liquid-phase epitaxy or hydrothermal epitaxy

Substrate: (111) $Gd_3Ga_5O_{12}$

Growth temperature: 500-520°C

Applications: Bubble generators, logic devices, and shift registers. A major application is the design of mass memories. Noncubic garnets are extremely attractive because of feasibility of growing thin films.

Comments: The eventual application of magnetic bubble devices to mass memories is dependent on the availability of thin films of materials which have to be uniform and free of defects. Normally, the imperfections in the crystal interface with the propogation of bubble domains in these devices are responsible for the collapse of the domains while deflecting them away from the circuits. Space growth of thin films, free of defects has a large potential for useful practical devices.

11. 3. e) MATERIALS FOR RADIATION DETECTORS

In a recent article, Putley (ref 63) reviews the more significant advances which have occured recently and discusses the factors governing the choice of detector for specific applications. The development of infrared detectors has followed two general lines: firstly, improvements in detectors with the highest performance, involving cooling; and secondly, the development of detectors with lower or no cooling requirements.

The first group of infrared detectors to be developed was the thermal detectors. These employ materials possessing some strongly temperature-dependent properties. The incident radiation raises the temperature of the detecting element producing a change in the property being used to detect the infrared radiation. The thermopile and the bolometer are typical examples of detectors of this kind.

In the second main group of detectors, the infrared radiation induces an electronic transition which leads to a change in electrical conductivity (photoconductivity) or to an output voltage appearing across the terminals of the device, as in photovoltaic devices.

There is an increasing interest in detectors requiring less cooling or no cooling at all, even if they have lower performance, which may lead to systems with greater cost-effectiveness. The two detectors in this class are the pyroelectric thermal detectors using triglycine sulphate and photoconductive detectors using (HgCd)Te optimized for 3-5 μm region at -80^{0}C and above. It has been shown by Morten (ref 64) that performance of triglycine sulphate is better for frequencies below 1 KH_z, and that of HgCdTe better above that frequency. The low frequency performance of tryglycine sulphate is of particular advantage in space applications where modulation is provided by rotation, or where the provision of high frequency modulation would consume too much power.

Materials in Use

HgCdTe, Triglycine sulphate, InSb, GaAs (uses n-type epitaxial film, not available commercially), Germanium, Silicon, Thallium Selenide-p-type, PbSnTe and PbSe.

Data On Materials For Radiation Detectors

$Pb_xSn_{1-x}Te$ (ref 65,66)

Growth method: Vapor phase epitaxy, liquid epitaxial growth (ref. 66)

Growth temperature: $\sim 500^{\circ}C$

Substrate: PbTe, PbSnTe

Applications: Radiation detectors, photovoltaic diodes

Comments: The effect of constitutional super-cooling during the solution growth is a serious deterrent to microelectronic processing of this material. Longo (ref 66) has discussed that constitutional supercooling can be prevented by controlling the following parameters: the temperature gradient across the growth interface, the melt thickness growth temperature, and cooling rate. This material has a large potential to be improved in low-gravity and may be used commercially in the future.

Triglycine Sulphate (TGS) (ref 67,38)

Growth method: Aqueous solution

Evaporation temperature: 30°C

Cooling rate: 0.1 - 0.25°C/day

Applications: Pyroelectric detectors, tuners. The crystals are the basis of advanced sensor system for new applications which include:

1) earth resources surveying
2) pollution monitoring
3) thermal imaging for medical diagnostics
4) fire location
5) infrared astronomy

Comments: Present acqueous solution growth techniques in the presence of gravity results in crystals with flaws and inclusions of solvent. Polishing and lapping of crystals to a few tens of microns thickness results in surface imperfections. Cutting introduces strain and defects which modify the ferroelectric properties and degrade the device behavior. The growth of this material in space should yield large, flawless crystals. The method of slowly lowering temperature of saturated growing solutions is suitable for the possible growth of lamellar, thin crystal with natural faces perpendicular to the polar axis. This elimination of polishing and lapping would enhance the yield, strength, surface perfection and mechanical strength. (ref 67)

InSb - Indium Antimonide (ref 69,70,71)

Growth method: Horizontal Bridgman, zone melting

Melting point: 525°C

Applications: Infrared filters & detectors, transistors

Comments: Thermal gradients necessary for crystal growth lead, in the presence of gravitational forces, to thermal convection which in general causes uncontrolled variations in the solidification rate and in diffusion boundary layer thickness and macroscopic segregation inhomogeneities. Skylab results (ref 70,71) indicate that ideal steady state growth and segregation were achieved leading to three-dimensional chemical homogeneity on a microscale dimensions. InSb detectors have low specific detectivity (ref 63) but can be used to monitor high intensity CO_2 lasers. This material is not suitable when a high sensitivity is required.

PbSe (Lead Selenide) (ref 64,68)

Growth method: Liquid epitaxial growth

Growth temperature: 325-400°C

Substrate: BaF_2 or SrF_2

Applications: Infrared detection. This material offers an advantage over PbTe because its smaller energy gap permits detection over the whole 3-5 μm atmospheric window.

Comments: This is the most useful detector available in the 3-5 μm range along with InSb. PbSe detectors have the disadvantage of relatively long time constant compared with the typical value obtained with HgCdTe. PbSe is a promising material for the future commerial use.

Quartz (bulk) (ref 72)

Growth method: Hydrothermal method

Growth temperature: 374°C crystallization temperature

Growth rate: 2.5 mm/day on a surface within 5° of basal (0001) plane

Applications: Filters, oscillators, tuners

Comments: High acoustic loss in hydrothermally grown synthetic quartz severely degrades its usefullness especially for high frequency applications. Techniques for obtaining high Q at high growth rates have obvious economic advantages. This material has large commercial value and can be improved in low gravity.

Ge - Germanium (bulk) (ref 50)

Growth method: Czochralski, float zone

Growth temperature: $\sim 936^\circ$C

Applications: Large germanium crystals can be used for detectors in gamma ray cameras, which has wide application in radiological studies of organs and vascular flow and other microwave devices.

Comments: The methods are already available to grow very high purity germanium crystals in earth-based laboratories. The manufacture of large high-quality crystals (i.e., free of imperfections) will be significantly affected by the fluid flow in the melt and reduced thermal convection in zero-gravity. This may permit larger and more perfect crystals.

1. 3. f) MATERIAL FOR ENERGY CONVERSION DEVICES

In the present study, only those materials are considered which are needed for photovoltaic conversion devices. Recently Herwig (ref 73) has reported about the solar research and technology. In this time of rising concern over energy, it will be appropriate to consider materials which can be improved by low-gravity environment growth, for efficient energy conversion devices.

Photovoltaic Conversion

The general objective at present is to develop low-cost, long lived, reliable photovoltaic conversion systems to be commercially available for a variety of terrestrial applications. The more specific objectives are to reduce the cost of solar cell arrays made from single crystal silicon wafers by a factor of more than 10 and to investigate the alternate solar cell technologies (for example, Cds, GaAs, thin film polycrystalline silicon showing low cost potential).

The use of semiconductor photovoltaic cells, or solar cells, for direct conversion of solar radiation to electrical power was demonstrated by Chapin, et. al., (ref 71). The reciprocal effect to electroluminescence which converts electrical energy to radiation is the photovoltaic effect. To obtain the photovoltaic effect, combination of transparent semiconductor materials, or semiconductor and thin film metal materials, are placed in intimate contacts to form junctions. These junctions introduce internal fields that, in the presence of light to produce electrons and ions, give rise to a potential difference and electric current, when an external circuit is closed. As long as there is a source of light of appropriate wavelength, the device serves as an effective small battery, or generator, delivering direct current electric power.

The studies made by Tsaur, et. al., (ref 26) indicate that GaAs as a solar cell material has the following advantages over Silicon:

1) the bandgap is a better match to the solar spectrum, therefore higher efficiencies than for Si may be anticipated

2) the decrease in power output with increasing temperature for GaAs is about half that for Si cells because the larger bandgap allows higher temperature operation

3) the GaAs cells achieve their performance with lower lifetimes and lower diffusion lengths than Si cells. Therefore they are less affected in performance by electron and proton irradiation effects that can reduce the performance of Si solar cells

4) the larger bandgap of GaAs produces a higher output voltage per cell than for Si which may be slightly helpful in some applications, although the current per cell is smaller

5) the optical absorption edge of GaAs is steep (because it is a direct-gap material) and causes most of the photon-induced carriers to be created within a micrometer of the illuminated surface. Since the minority carrier diffusion lengths in GaAs tend to be small, cells must be designed with very thin front layers and multi-finger front-contact grids must be used to keep the internal resistances low. The problem is compounded by the fact that the surface recombination velocity of GaAs tends to be high, 10^6 - 10^7 cm^{-1} (compared with values of the order of 10^5 cm^{-1} for Si solar cells). Hence a high built-in field is essential in the thin ($\sim$ 0.3 μm) front layer to sweep the minority carriers away from the surface towards the junction to minimize surface recombination loss.

6) the density of GaAs is 5.31 g cm^{-3} whereas that of Si is 2.33 g cm^{-3}. This is a considerable disadvantage in achieving comparable power-to-weight ratios for the two materials for the same cell thickness.

7) the cost of GaAs is at least 20 times that of Si. This can add up to $10 to the cost for a 1 x 2 cm cell.

An important factor in favor of the GaAs cells is their superior performance under most irradiation conditions.

Materials in Use

The other photovoltaic materials that can be considered as alternatives to the use of silicon are thin film hetrojunction materials, (such as cadium sulphide and copper sulphide), homojunction materials (such as gallium arsenide) and metal semiconductor junctions, (such as Schottky barrier diodes). According to Herwig (ref 73) solar cells using Cds-CuS seem to present the most interesting alternative approach to Silicon solar cell at this time

Improvement in the crystal quality of these materials can be of considerable significance in the research and technology in photovoltaic conversion techniques.

Data for Materials for Energy Conversion Devices

Cu_2S-CdS (ref. 50, 73)

Growth method: Cu_2S layers were grown by displacement reaction in aqueous solution of Cu^{+2}.

Growth temperature: 75°C

Growth period: A growth period of 30 minutes was sufficient to form a layer of 10μm.

Substrate: CdS crystals grown by vapor transport

Applications: Heterojunction photovoltaic cells for energy conversion devices.

Comments: According to Herwig (ref. 73) CuS-CdS cells seem to present the most interesting alternative approach to silicon cells. Improvement in the crystal quality can play an important role in the successful and efficient photovoltaic conversion devices.

CdS - Cadmium Sulphide (ref. 76, 77)

Growth method: Chemical vapor transport, Evaporated Films, solution spraying.

Applications: Solar cells

Comments: Thin film CdS solar cells have been fabricated. Solar cells however are the most important long-duration power supply for satellites and space vehicles. Other materials in this groups seems to have more promise than CdS.

PART III

CONSOLIDATED TABLES

OF

CANDIDATE MATERIALS

Note: Materials marked by an asterick in each category are the recommended candidates for growth in space.

TABLE NO. 1

APPLICATIONS	MATERIALS IN USE	TYPE OF GROWTH						COMMENTS	REF.
		CHEMICAL VAPOR PHASE EPITAXY	LPE	BRIDGMAN	CZOCHRALSKI	FLOAT ZONE	OTHER		
Electro-optic Devices	$Bi_4Ti_3O_{12}$ Bismuth Titanate *						r.f. sputtering	Used for electro-optical switching, optical display, and memory applications	14
	$Ba_xSr_{1-x}Nb_2O_6$ Barium Strontiam Niobate				X			Low voltage deflectors, non-linear optics	15
	$Ba_2NaNb_5O_{15}$ Barrium Sodium Niobate				X			Same as $Ba_xSr_{1-x}Nb_2O_6$	15
	ZnO (films) Zinc Oxide	X						Electro-optic and acousto-optic interaction devices	16
	α-$LiIO_3$ Lithium Iodate						Solution Method (slow evaporation)	Second harmonic geveration	17

TABLE NO. 1 (continued)

APPLICATIONS	MATERIALS IN USE	TYPE OF GROWTH						COMMENTS	REF.
		VAPOR PHASE EPITAXY	LPE	BRIDGMAN	CZOCHRALSKI	FLOAT ZONE	OTHER		
Electro-optic Devices	$LiNbC_3$ Lithium Niobate *		x		x			Light modulators, optical data processing, wave guide & SHG	18,19 20,21
	GaAs Gallium Arsenide * (bulk)			x	x	x		Light-emitting diodes, substrate for epitaxial films	22,23 25,28
	GaP Gallium Phosphide*	x						Has a potential use as an electro-optic modulator of visible radiation. LED	13,25 30
	$GaAs_{1-x}P_x$	x						Electro-luminescent diodes, room temperature injection lasers & photocathodes	25,31 32
	YAG Single Crystals *				x			Optical lasers & jewelry	33

TABLE NO. 1 (continued)

APPLICATIONS	MATERIALS IN USE	TYPE OF GROWTH						COMMENTS	REF
		CHEMICAL VAPOR PHASE EPITAXY	LPE	BRIDGMAN	CZOCHRALSKI	FLOAT ZONE	OTHER		
Electro-optic Devices	YVO_4 Yittrium Vandate				x	x		Laser, optical & infrared windows	34,35,36
	$CaCo_3$ * Calcite						Traveling solvent method	Optical work, polarized light	37
	$K_{0.5}Na_{0.5}NbO_3$						Molten Solution	Computers, IR sensors, lasers, radar & sonar devices	

TABLE NO. 2

APPLICATIONS	MATERIALS IN USE	TYPE OF GROWTH						COMMENTS	REF
		CHEMICAL VAPOR PHASE EPITAXY	LPE	BRIDGMAN	CZOCHRALSKI	FLOAT ZONE	OTHER		
Semi-conducting Devices	$In_{1-x}Ga_xP$ *	x						Injection laser diodes, electroluminescent diodes	75,49
	$Al_xGa_{1-x}As$ * (p-type)	x	x				Molecular beam epitaxy	LED, hetrostructure lasers, Integrated optics	46
	Si (bulk) Silicon				x	x		Semiconductor devices, IR windows, substrates	49
	Si (films) Silicon	x						Semiconductor devices, monolithic integrated circuits	51,52
	Si (polycrystalline) Silicon						Vacuum deposition pyrolysis	Diodes, MOS devices, solar energy collectors	54,55,56
	Ge (bulk) Germanium				x	x		Detectors in gamma ray detectors & other microwave devices	50
	GaAs Gallium Arsenide *	x	x					Unique for many devices. High temperature transistors, field effect transistors	22,23,25 28

TABLE NO. 2 (continued)

APPLICATIONS	MATERIALS IN USE	TYPE OF GROWTH						COMMENTS	REF.
		CHEMICAL VAPOR PHASE EPITAXY	LPE	BRIDGMAN	CZOCHRALSKI	FLOAT ZONE	OTHER		
Semiconducting Devices	GaP Gallium Phosphide *	X						Schottky barrier diodes, secondary emission dynokes	13,25 30
	InSb Indium Antimonide			X		X		IR filters & detectors and transistors	69,70 71

TABLE NO. 3

APPLICATIONS	MATERIALS IN USE	TYPE OF GROWTH						COMMENTS	REF.
		CHEMICAL VAPOR PHASE EPITAXY	LPE	BRIDGMAN	CZOCHRALSKI	FLOAT ZONE	OTHER		
Acousto-optic Devices	$LiNbO_3$ Lithium-niobate				X		Epitaxial growth by melting (EGM)	Acousto-optic devices	57
	$PbMoO_4$ Lead Molybdate *				X			Has higher figure of merit than $LiNbO_3$. Also has low loss for applications below 0-5GH_z	57
	GaP Gallium phosphide	X							57
	ZnO (films) Zinc oxide	X						Films are grown on sapphire substrate. Acousto-optic interaction devices	16

TABLE No. 3 (continued)

APPLICATIONS	MATERIALS IN USE	TYPE OF GROWTH						COMMENTS	REF.
		CHEMICAL VAPOR PHASE EPITAXY	LPE	BRIDGMAN	CZOCHRALSKI	FLOAT ZONE	OTHER		
Acousto-optic Devices	α - TeO_2 Paratellurite*						Hydrothermal	High efficient acousto-optic light deflectors have been made figure of merit 21 times of $PbMoO_4$	59

TABLE NO. 4

APPLICATIONS	MATERIALS IN USE	TYPE OF GROWTH						COMMENTS	REF.
		CHEMICAL VAPOR PHASE EPITAXY	LPE	BRIDGMAN	CZOCHRALSKI	FLOAT ZONE	OTHER		
Magnetic memory Devices	$Sm_{0.55}Tb_{0.45}$ FeO_3 Orthoferrite						Flux method	The coercivity of these crystals is too high to be useful. The large domain size can be decreased by reducing the anisotropy	61
	Fe_5LiO_8 Lithium ferrite spinel						Flux method	Bubble memory devices. Difficult to prepare platelet in 1-g. unnecessary cutting and polishing can be avoided.	61
	BiCaVIG Garnet *						Flux method	Computer memories and display devices	61
	YCaVIG						Flux method	Computer memories and display devices	61
	$Gd_xY_{3-x}Ga_y$ $Fe_{5-y}O_{12}$ Garnets *		X				Hydrothermal epitaxy	$Gd_3Ga_5O_{12}$ was used as a substrate. Used for bubble generators, logic device, mass memories. These are extremely attractive because of feasability of growing thin films.	61

TABLE NO. 5

APPLICATIONS	MATERIALS IN USE	TYPE OF GROWTH						COMMENTS	REF.
		CHEMICAL VAPOR PHASE EPITAXY	LPE	BRIDGMAN	CZOCHRALSKI	FLOAT ZONE	OTHER		
Radiation Detectors	TGS Triglycin-sulphate *						Acqueous solution	Pyroelectric-detectors, tuners, sensors for earth resources surveying and medical diagnostic Present growth results crystals with flaws. Has a great potential for improvement	56, 57
	$Pb_xSn_{1-x}Te$ *	X	X					Photovoltaic diodes. Can be improved in low-gravity environment.	54, 55
	PbSe Lead Selenide *		X					IR detection. Has a advantage over PbTe because of its smaller energy gap which permits detection over the whole 3-5μm atmospheric window	
	InSb Indium Antimonide			X		X		IR filters and detectors, transistors can be used to monitor high intensity CO_2 lasers. They have low specific detectivity.	65, 66, 67

TABLE NO. 5 (continued)

APPLICATIONS	MATERIALS IN USE	TYPE OF GROWTH						COMMENTS	REF.
		CHEMICAL VAPOR PHASE EPITAXY	LPE	BRIDGMAN	CZOCHRALSKI	FLOAT ZONE	OTHER		
Radiation Detectors	Quartz (bulk)						Hydrothermal growth	Filters and tuners Has large commercial value	72

TABLE NO. 6

APPLICATIONS	MATERIALS IN USE	TYPE OF GROWTH						COMMENTS	REF.
		CHEMICAL VAPOR PHASE EPITAXY	LPE	BRIDGMAN	CZOCHRALSKI	FLOAT ZONE	OTHER		
Energy Conservation Devices	GaAs Gallium Arsenide *	X	X					GaAs as a solar cell material has many advantages relative to Si. They can perform well under most irradiation conditions.	63
	Si (films) Silicon	X					Implant epi-process	Semiconductor devices, photovoltanic cells	49, 50
	Si Silicon (polycrystalline films)						Vacuum deposition	Solar energy collectors in the harnessing of solar energy	51, 52
	Cu_2S-CdS *						Acqueous solution	Heterjunction photo cells. According to Herwig Cu_2S-CdS seems to present the most interesting alternative approach to Si-cells.	68
	CdS Cadmium Sulphide	X						For solar cells	76

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APPENDIX I

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