**Five aspects of gradient index optics have been investigated. The possibilities of making gradient index germanium by alloys with silicon have been shown. This represents the first time that prescribed index gradients have been made in germanium. Second, methods have been developed for the measurement of the gradient index materials in the infrared portion of the spectrum. Third, initial work has been conducted on the analytic methods necessary for describing the performance of optical systems which have gradients without rotational symmetry. Fourth, six lens elements have been fabricated (Nood**
lenses) and their profiles measured. Finally, an assessment of the current technologies in gradient index has been made. This includes a series of recommendations which will be necessary to complete to make gradient index systems useful for Army applications.
## CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Gradient Index Germanium</td>
<td>1</td>
</tr>
<tr>
<td>A. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>B. Materials</td>
<td>4</td>
</tr>
<tr>
<td>C. Gradients Fabrication</td>
<td>6</td>
</tr>
<tr>
<td>D. Segregation</td>
<td>8</td>
</tr>
<tr>
<td>E. Refractive Index as a Function of Composition</td>
<td>14</td>
</tr>
<tr>
<td>II. Infrared Materials Testing</td>
<td>17</td>
</tr>
<tr>
<td>III. Ray Tracing in Anamorphic Gradient Index Media</td>
<td>20</td>
</tr>
<tr>
<td>IV. Fabrication of Six Gradient Index Samples</td>
<td>27</td>
</tr>
<tr>
<td>V. Technology Assessment</td>
<td>28</td>
</tr>
<tr>
<td>A. Design of Gradient Index Systems</td>
<td>36</td>
</tr>
<tr>
<td>B. Materials</td>
<td>38</td>
</tr>
<tr>
<td>C. Measurements</td>
<td>43</td>
</tr>
<tr>
<td>D. Production Capability</td>
<td>43</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>45</td>
</tr>
</tbody>
</table>
I. Gradient Index Germanium

A. Introduction

In an effort to find alternatives to complex multi-element and aspheric element imaging systems, interest in gradient index optics has surged in the past decade. Gradient index, as the name implies, involves using materials in which the index of refraction varies as a function of spatial coordinate. Through the use of such materials, the imaging properties of lenses can be enhanced, if the proper gradient is chosen. Gradient index optics presents the lens designer with extra degrees of freedom for use in the correction of aberrations.

There are three basic requirements for the useful manufacture of gradient index lenses: (1) Fabrication of gradient index materials, (2) measurement of gradients, and (3) the ability to design gradient index lens systems. In extending the previous work done in gradient index optics into the infrared, the last two requirements can be met by direct extensions of previous work. In contrast, the fabrication of gradient index materials in the infrared is, in general, quite different from any work previously done.

The effects of various types of index gradients on the imaging properties of lenses has been sufficiently well analyzed [1-7] to allow for a basic understanding of what can and cannot be done with gradient index lenses, aside from any lack of technology for making a particular gradient. Through the use of gradient index lens design programs [8,9] it is possible to design gradient index lenses and investigate the effects of different gradient profiles on imaging quality. Although there are still many limitations on the usefulness of these programs, the basic tools for designing gradient index lenses are available.

There are a vast number of materials which are transparent in various regions of the infrared spectrum [10-16]. The two major materials which form the basis of this investigation are germanium and silicon. Since both of these elements lie in the same column of the periodic table, Group IV, they have many common properties which make them good candidates for preliminary work. They are both semiconductors which form crystals of the diamond structure with totally covalent bonding, and are both transparent over a large and overlapping region of the infrared spectrum. Since these two elements are so similar it is possible to form an alloy in any desired ratio. The fact that they have differing refractive indexes, 3.4 for silicon and 4.0 for germanium, makes them ideal candidates for making gradient index materials.

Some investigations have been made into the properties of germanium-silicon alloys, but mostly from the aspect of semiconductor and solid state research. No attempt has been made to characterize the index of refraction of any such alloy as a function of composition. Properties such as lattice constant, density, band gap and band structure have all been studied as a function of alloy composition [17-21]. Electrical [22] and some optical [23]
properties have also been measured. Braunstein et al investigated the optical absorption in varying alloys. Their work includes the region of the spectrum near the band gap. These experiments were done to provide a way of substantiating predicted changes in the band structure with alloy composition.

The general band structure of germanium-silicon alloys is similar to the band structure of the two constituents. At a concentration of approximately 15% silicon, the band structure changes over from a germanium-like to a silicon-like band structure. Figure 1 shows the ways in which the band gap changes as a function of composition. Since there has been no work done to determine index of refraction as a function of composition, the best place to start is with an analysis of the absorption spectra of such alloys. Through a Kramers-Kronig analysis it is possible to estimate changes in refractive index. Since germanium and silicon contain only covalent bonding there is little absorption at all wavelengths below the fundamental absorption edge. In ionic crystals, absorption in the far infrared is attributed to lattice vibrations caused through the interaction of the field with the ionic bonds, further complicating any calculations involving combinations of alkali-halides. Consequently the change in real index of refraction of Ge-Si alloys throughout the spectral region below the band edge can be estimated through a Kramers-Kronig analysis of the changes in the absorption spectra above the band edge.

A method is needed for making such alloys into a gradient. By establishing techniques of crystal growing it is possible to make a material in which the concentration of silicon will vary as a function of length [24,25]. This technique for making gradients is radically different from any techniques previously used for the fabrication of gradient index materials. The specific crystal growing technique used is based on work originally done by Czochralski [26].

In the Czochralski crystal growing scheme a capillary tube or seed crystal is lowered into the crucible containing the melted material. The material attracted into the capillary tube solidifies as a single crystal seed. This is then slowly withdrawn as material begins to crystalize onto the seed. By varying the temperature or rate of withdrawal the diameter of the crystal can be controlled. The original melt contains mostly one or the other of the two elements and only a small concentration of the second element, called the dopant.

A gradient in concentration is formed because of the different melting points of the two materials. The ratio of the concentration of the materials in the crystal to that of the melted material at the crystal-melt interface is known as the segregation coefficient. For germanium it is 5.5 [28]. This phenomenon of segregation tends to pull out a higher or lower concentration of dopant than is in the melt, depending on whether the segregation coefficient is greater or less than one, respectively. There are various ways in which this technique can be used to control the gradient in the material.
Figure 1. Band Gap and Refractive Index vs. Alloy Composition.
B. Materials

There are a wide variety of materials which are commonly used as optical materials in the infrared region of the spectrum. Some of these are outlined in various categories on the following page. Most of these materials have some possibilities for use in gradient type systems using one technique or another for the fabrication of the gradient index material.

In the first category are the glasses. Many of the standard optical glasses which are used in optical systems in the visible portion of the spectrum also transmit into a limited region of the near infrared (0.8-2.0 μm). There are also other glasses such as the doped selenium glasses and other arsenic, sulfide and selenium combinations. Most of these glasses have the potential for use as gradient index materials by using the techniques currently used for fabrication of gradient materials. The most prevalent technique to be used in glasses is to do an ion diffusion at elevated temperatures. This technique of gradient fabrication is the only one that has been used for production of gradient materials on a large scale. Glasses cannot in general be used in the Czochralski technique for fabrication of gradient index material and must have gradients formed using other methods.

The next three categories all involve crystalline solids. The category of miscellaneous crystals contains materials which would not be easily formed into gradient materials using the techniques discussed in this report. The main problems here arise from the fact that it is very difficult to grow homogeneous crystals of these materials, either due to the nature of the solid or because of the higher temperatures which would be involved.

Most of the alkali-halides and some of the semiconductor crystals which are transparent in the infrared would be good candidates for fabrication of gradient materials using a Czochralski crystal growing scheme. Depending on the material being used for the base or hot material the refractive index may be varied by use of a dopant which combines with the host on a substitutional or interstitial basis. In the first case the dopant interacts with the host lattice in such a way that the dopant atom replaces a host atom one for one in the crystal lattice. The latter case involves either the trapping of the dopant atom inside the lattice of the host, or else an actual breakdown of the lattice in the region of the dopant atom. These different doping schemes will be elaborated on later.

The semiconductor crystals have some advantages over the alkali-halides. The alkali-halides tend to be much more delicate materials than the semiconductors. They tend to be softer than semiconductors which has certain disadvantages in handling and use. The alkali-halides also tend to be hygroscopic. This presents many problems in preparation and handling of samples; it becomes difficult to grind and polish optical surfaces. The materials must also be kept in controlled environments after polishing to avoid absorption of moisture and subsequent surface damage. These things aside, the use of alkali-halides for gradient fabrication using Czochralski crystal growing techniques could prove to be very rewarding. The feasibility of forming a gradient using alkali-halides has been demonstrated in a NaCl-KCl sample and in a Ge-Si sample.
Table 1. Infrared Materials

1. Glasses - fused silica, arsenic modified selenium, arsenic trisulfide, etc.
2. Alkali Halides - potassium chloride, sodium chloride, silver chloride, potassium iodide, etc.
3. Semiconductors - germanium, silicon, indium antimonide, gallium arsenide, zinc selenide, etc.
4. Miscellaneous Crystals - diamond, sapphire, crystal quartz, etc.
5. Miscellaneous Amorphous - selenium, etc.
The semiconductors seem to show the most promise for formation of infrared gradient index materials. Zinc sulfide-zinc selenide combinations have been formed into gradients using chemical vapor deposition techniques. Germanium-silicon alloys have been formed into gradient index materials using Czochralski growth and have been the basis for most of the work done on forming gradients through crystal growing techniques. There are many reasons for choosing this binary combination as the basis for preliminary work. Both materials have identical crystal structure, thus operating on a substitutional basis. They have relatively close lattice constants, large overlapping regions of transparency, different indices of refraction and neither of the materials is hygroscopic. All of these properties make this pair a good combination for preliminary work. The last category consists of materials which do not show much promise for use in gradient index infrared optics.

The important properties of germanium and silicon are outlined in Table 2. Both materials are of Group IV elements of the periodic table along with carbon. Therefore, it is not surprising that the crystal structure is an extension of the face-centered cubic structure with totally covalent tetrahedral bonding. The crystal structure is the same as that of crystalline carbon, namely diamond structured. The fact that the bonding and crystal structure is identical in the two materials is a great advantage. Covalent bonds are much stronger than ionic bonds; therefore, many of the problems of induced stresses causing sample fracture upon cooling are alleviated. Also the atoms can substitute for one another on a one-to-one basis without disrupting the crystal structure. A further advantage is gained by the fact that the lattice constants for the two materials differ by only about 4%, and the ratio of lattice constants is relatively stable as a function of temperature.

It is important that both materials are infrared transmitting over large overlapping regions of the spectrum. Germanium begins transmitting below its band edge at about 2 μm and silicon transmits at wavelengths longer than 1.2 μm. The two materials are commonly used optical materials and can be cut, ground and polished without taking extra precautions; they are actually easier to polish than many optical glasses. Neither material is hygroscopic and both are semiconductors. The refractive indices are quite different, which is another important consideration in trying to allow two materials to form an index gradient. The last important properties of these materials are their phase properties. They have well separated melting points with very simple phase properties. This is important for simplifying the calculations of index profile for gradients grown using segregation effects.

C. Gradient Fabrication

In general, the techniques of crystal growing are well established and understood. The use of these techniques is usually limited to purification and production of single crystal materials. Although these methods are used in some schemes for doping semiconductors, the goal is usually to produce a homogeneous material. Subsequently, not a great deal of work has been done to produce and control the nature of inhomogeneous materials.
Table 2. Properties of Germanium and Silicon

A. Common Properties
1. Group IV of the Periodic Table
2. Totally Covalent Bonding
3. FCC - Crystal (Diamond Structure)
4. Semiconductors
5. IR Transmitting
6. Not Hygroscopic

B. Other Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Germanium</th>
<th>Silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Constant</td>
<td>5.65 Å</td>
<td>5.43 Å</td>
</tr>
<tr>
<td>Density</td>
<td>5.32 g/cm³</td>
<td>2.33 g/cm³</td>
</tr>
<tr>
<td>Melting Point</td>
<td>937°C</td>
<td>1412°C</td>
</tr>
<tr>
<td>Index @ 10.6</td>
<td>4.0</td>
<td>3.4</td>
</tr>
<tr>
<td>Intrinsic Resistivity</td>
<td>50 Ω-cm</td>
<td>1000 Ω-cm</td>
</tr>
</tbody>
</table>
The method used for fabrication of gradient index materials is based on the use of a crystal growing scheme due originally to Czochralski. The crystal growing apparatus consists of an R. F. induction heating unit, a sealed envelope to maintain the melted material and crystal under an inert atmosphere during the crystal growing process, and a hydraulic pulling mechanism and stepper motor drive for pulling the crystal from the melt. The system allows for variable pulling and rotation speeds during the pulling process. The variable rotation speed can be used for varying the amount of agitation in the melt, thereby controlling the homogeneity of the melt. The pulling speed and melt temperature effect the crystal diameter, and if varied as a function of time the gradient profile is subsequently altered. The basic system is illustrated in Figure 2.

The index or equivalently the composition gradient is formed along the length of the crystal. The gradient arises due to a natural effect known as segregation. The important thing to note at this time is that the surfaces of constant index are the surfaces which represent the interface between the growing crystal and the melt. These surfaces are isothermal surfaces at the time of crystal formation, and are therefore not required to be planar. In general they are of the shape shown in the diagram due to the fact that the radiative cooling from the sides of the crystal tends to cool the outside surface more rapidly than the central core. Heat is also dissipated up through the seed crystal and pulling rod. Since the outside of the crystal is cooler, we not only have an axial temperature gradient, but also a radial temperature gradient.

It is possible to vary the radial temperature distribution by adding auxiliary heat into the sides of the crystal. This has the net effect of balancing the radiative heat losses to varying degrees. These effects have been demonstrated in the crystal grower. The ultimate limit as to how well the temperature gradients can be controlled is ultimately equivalent to the problem of how well the temperature gradients can be controlled during the growing process. This is a difficult problem which has not been solved and needs further investigation, and is a much more challenging problem than that of controlling the actual index profile as a function of length. Figure 3 illustrates the general functional form of the index of refraction profile.

D. Segregation

In the techniques which have been attempted to date, the phenomena of segregation is the primary contributor to the formation of a gradient during the process of Czochralski crystal growth. In order to demonstrate exactly how the effect of segregation in crystal growth occurs, it is necessary to understand the phase properties of the materials which are being used. The simplest binary system which best illustrates how the phase properties of a compound affect the resultant crystal, is one in which the phase diagram for the materials is "lens" shaped. This is a term used to describe phase diagrams of the form illustrated in Figure 4, where one sees the phase properties of germanium and silicon plotted as a function of composition. The left most side corresponding to pure germanium (i.e. 0% Si) and the right most side corresponding to pure silicon. The abscissa is temperature in °C.
Figure 2. Czochralski Crystal Growing.
\[ r^2 = x^2 + y^2 \]

\[ z = \text{OPTICAL AXIS} \]

\[ N(r,x) = N(z - f(r)) \]

Figure 3. "Conical" Gradients.
Figure 4. Germanium-Silicon Phase Diagram.
The phase diagram can be broken into three distinct regions. The upper region corresponds to a pure liquid state. The lowest region corresponds to a pure solid state, and the intermediate region is in some linear superposition of liquid and solid states. One sees that at each end of the graph the intermediate state disappears. This is because both germanium and silicon have well defined melting points. These are 935°C for germanium and 1410°C for silicon. The descriptive name given to this type of binary compound is based on the shape of the central region.

In order to illustrate the effect of segregation, it is instructive to trace an isothermal line across the phase diagram. This isothermal line corresponds to an isothermal surface which occurs intermediate to the crystal and the melt during the pulling process, as illustrated in Figure 5. Above the isothermal surface is the solid crystal, and below is the molten crystal melt. If one draws the isothermal line on the phase diagram so that it intersects the upper curve at the point corresponding to the concentration of silicon in the melt, \( C_L \), one can then trace the isothermal line across to see where it intersects the lower curve and consequently find the concentration of silicon, \( C_S \), in the solid state. This result implies that silicon tends to be removed or crystallized more rapidly than the germanium. This is an expected result since the melting point of silicon is so much higher than germanium.

A direct result of this effect is that a gradient is formed down the length of the crystal, parallel to the pulling direction. Since the silicon is depleted from the melt more readily than the germanium, the concentration of silicon in the melt tends to decrease as a function of the crystal length. This subsequently reduces the concentration of silicon in crystal as a function of length in an identical manner. This use of a naturally occurring effect to form a gradient during the growth of a crystal is not the only method of forming a gradient using the Czochralski technique.

It should be possible to use a "floating crucible technique" \([29]\) to produce gradients in which the concentration in the crystal is identical to the melt, and the melt concentration can be controlled dynamically by addition of either the dopant or major constituent. This technique and others should be investigated in the future because of the promise of much greater control over the index profile.

It is informative to investigate what type of concentration profile can be expected under simplified assumptions. If it is first assumed that the segregation coefficient remains constant throughout the growth period of the crystal, and secondly that the melt is perfectly homogeneous, then a simple relation exists which defines the concentration profile of the dopant. The first assumption is valid for low dopant concentrations, and the value is given by drawing tangents to the two curves at the lower limit and tracing an isothermal line through these lines. The second approximation is valid if the melt is sufficiently well agitated, and the crystal is grown sufficiently slow, so that any change of dopant concentration in the melt changes the concentration uniformly throughout the melt. Under these assumptions, it can be shown that the concentration in the crystal has the following dependence;
Figure 5. Czochralski Crystal Growing.
\[ C(s) = K C_0 (1-s)^{k-1} \] 

(1)

where,

- \( C \) = concentration of dopant in crystal
- \( K \) = segregation coefficient
- \( C_0 \) = initial dopant concentration in the melt
- \( s \) = fraction of material which has crystalized

This concentration profile has been plotted in Figure 6 for silicon in germanium, \( k = 5.5 \). Since the segregation coefficient is greater than one, we see that the silicon is rapidly removed from the melt as the crystal is grown. The concentration of silicon is down by an order of magnitude after only 40% of the material has crystallized. Therefore, for the above approximations and Equation 1 to be valid, the melt must be rapidly stirred, or else the crystal must be grown relatively slowly to allow the concentration of silicon to remain uniform throughout the melt. Typical pulling speed used is approximately 2-3 mm/hr. in comparison to growth rates for homogeneous germanium on the same system which are about 40-50 mm/hr. If this is not the case, the silicon in the region of crystal growth is rapidly depleted and the profile becomes more complicated.

Since the concentration profile depends on the percentage or fraction of material crystallized, it is possible to scale the profile spatially by changing the total amount of material or by changing the pulling rate. Other methods for controlling the gradient include active addition of silicon during the pulling process, changing the pull rate, and changing the melt temperature as a function of concentration in the melt, and therefore at higher dopant concentrations the profile will vary because the segregation coefficient changes with time. There are obviously many ways of controlling the gradient profile and with accurate means of control over the above mentioned variables, reproducibility should be good.

E. Refractive Index as a Function of Composition

Since there has been no work done to either calculate or measure the refractive index of germanium-silicon alloys in their region of transparency in the infrared, an attempt must be made to estimate the index of such materials as a function of wavelength and composition. One method for estimating the index of refraction is based on a Kramers-Kronig analysis. The Kramers-Kronig dispersion relations give the value of the real or imaginary index of refraction from an integral over all values of the other. Since some work has been done to measure the absorption spectra of such alloys above their band edge, it is possible to use this formulation to estimate changes in the index of refraction as composition changes. The dispersion relations are given by the following:

\[ n(\omega_0) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega K(\omega)}{\omega^2 - \omega_0^2} \, d\omega \] 

(2a)
Figure 6. Concentration Profile of Silicon in Germanium.

\[ g = \text{FRACTION OF MATERIAL CRYSTALIZED} \]

\[ C = \text{CONCENTRATION OF Si IN CRYSTAL} \]

\[ C_0 = \text{INITIAL CONCENTRATION OF Si IN MELT} \]

\[ k = \text{SEGREGATION COEFFICIENT} \]

\[ \frac{C}{C_0} = k (1 - g)^{k-1} \]

\[ k = 5.5 \]
\[ K(\omega_0) = \frac{-2\omega_p}{\pi} \int_0^\infty \frac{n(\omega)}{\omega^2 - \omega_0^2} \, d\omega \quad (2b) \]

where the P denotes the principal part of the integral, and;

\[ N_c = n + iK = \text{complex refractive index} \]
\[ n = \text{real refractive index} \]
\[ K = \text{extinction index} \]

The relation of interest is 2a. This is because the extinction index is directly related to the absorption, \( \alpha \).

\[ K(\lambda_0) = \frac{c}{2\omega} \alpha(\omega) \quad (3) \]

It was stated earlier that there is very little absorption below the band edge for both germanium and silicon of adequate purity, and this can also be assumed for any alloy of the two elements. Therefore, \( \alpha(\omega) = K(\omega) = 0 \) for \( \omega < \omega_{gap} = E_{gap}/h \). With these facts expression la simplifies to;

\[ n(\omega_0) = 1 + \frac{c}{\pi} \int_0^\infty \frac{\alpha(\omega)}{\omega^2 - \omega_0^2} \, d\omega \quad (4) \]

At wavelengths on the order of 10 microns or longer, the value of \( \omega_0 \) is down by an order of magnitude from the value of \( \omega_{gap} \). This accounts for the fact that the dielectric constant at 10 microns is close to the value measured at D.C. Therefore the expression can be further simplified in this region of the spectrum;

\[ n(\omega_0) = 1 + \frac{c}{\pi} \int_0^\infty \frac{\alpha(\omega)}{\omega} \, d\omega \quad (5) \]

In order to estimate expected changes in refractive index it is not necessary to quantitatively evaluate equations 4 or 5. If the refractive index of pure germanium and silicon is known, then it is possible to use these equations to predict changes in refractive index. Since the fastest changes in the band structure occur in the lowest conduction band, the major changes in the value of the absorption occur near the fundamental absorption edge. Indeed, the major change is that the band gap shifts in frequency.

In order to get some feeling for the types of changes to be considered, a crude calculation of index change follows. As a first approximation in trying to predict changes in refractive index as a function of composition, assume that the value of \( n(\omega_0) \) varies linearly with the band gap of the alloy. That is, ignore the dependancies of the integrand and assume that \( n(\omega) \) varies in the same way as \( \omega_{gap} \), the lower limit of the integral. An
estimate of the refractive index can then be made from experiments that have been done to measure the band gap as a function of composition. A plot of band gap and predicted refractive index are shown in Figure 1 as a function of composition. This leads to the following dependencies for the refractive index at 10 microns:

\[
\begin{align*}
0 - 15\% \text{ Silicon} & : \quad n = 4.003 - 0.0179 \% \text{Si} \\
0 - 85\% \text{ Germanium} & : \quad n = 3.418 + 0.00373 \% \text{Ge}
\end{align*}
\]

Although this is a crude approximation, it is not expected that the changes in refractive index will deviate very far from those predicted, because of the difficulties involved in obtaining large (10-15\%) concentration gradients.

One other consideration is the dispersion of these alloys. From the form of the integral in Equation (4), it is evident that as \( \omega_0 \) increases towards the band edge the contribution to the integral at low frequencies becomes more important. As the amount of silicon in an alloy increases the contribution from the lower frequencies is lost because the band gap shifts to higher frequencies. Since this is the portion which contributes the most to dispersion, the dispersion in higher silicon content alloys tends to be less than that of germanium rich alloys. This is also evidenced by the fact that the change in index of pure silicon from 2 - 10 microns is only about 40\% of the change in the index of refraction of germanium over the same spectral region.

II. Infrared Materials Testing

Due to the nature of the gradients formed in the crystal growing technique it becomes necessary to measure the properties of the gradient using destructive testing techniques. This is done by taking a slice of the crystal from the center of the cylinder parallel to the growth direction of the crystal. The sample must then be ground and polished to have plane parallel faces of optical quality. This is to insure that only material properties are measured and not surface properties. The parallelism of the sample can be measured in a goniometer or interferometer to assure adequate parallelism. For most purposes a goniometer which is accurate to a few seconds of arc is adequate. Presently only one technique has been proposed and tested for non-destructive testing of axial gradients. This technique is based upon certain assumptions which are not true for gradient index materials fabricated using Czochralski's crystal growth (i.e. Gaussian index profile in an axial gradient). At present the only methods for testing these types of materials are all destructive.

The first method of testing infrared germanium-silicon gradients was used for preliminary measurements to verify that a transparent material had been produced and that a gradient had been formed. This method involves preparation of the sample crystal as discussed, and then measuring the optical transmission as a function of wavelength and position along the length of the crystal. There is a two-fold purpose in conducting this measurement. This experiment gives some insight into the optical quality of the crystal and some measure of the gradient maximum silicon concentration.
The measurement is done by placing a slit which is 1-2 mm wide across the polished sample, perpendicular to the gradient direction. The sample transmission is then measured and plotted as a function of wavelength in a spectrophotometer. This measurement is done in the region of the fundamental absorption edge. For the germanium-silicon crystals, data was taken from 1.5 μm to 2.5 μm. Since germanium has such a high base refractive index, about 4.0, the surface reflections from a bulk sample amount to 60% of the incident energy. The transmission of a good quality crystal should be greater than about 35%. Very weak transmission implies either very large amounts of scattering or heavy absorption. These effects can be brought about through excess oxygen present causing absorption bands, or formation of Si-C which causes very strong scattering within the sample.

A series of these measurements can be taken along the length of the crystal. Figure 7 illustrates a set of such curves taken for gradient sample IR-3. It is evident from the plots that the absorption curve shifts to longer wavelengths as one looks further down the length of the crystal. This is an expected result since the composition should progress towards lower silicon content during the crystal pulling process, and the absorption edge for silicon is higher in energy than that for germanium.

The second method for testing infrared gradient index materials involves the use of a laser beam and a plane parallel sample with faces parallel to the direction of the gradient. The deflection of the laser beam upon passing through the sample normal to the first surface is a direct measure of the gradient slope. This is an important quantity for the specification of axial gradients because it is the magnitude of the gradient slope which determines the contribution of the gradient to third order aberration correction when used in an optical element. The expansion of the gradient along the z axis is given by:

\[ N(z) = N_{00} + N_{01}z + N_{02}z^2 \]

It can be shown that the value of \( N_{01} \) is given by:

\[ N_{01} = \frac{\theta}{t} \]

where \( \theta \) = angular deflection of the laser beam

\( t \) = thickness of the sample

With the use of a CO\(_2\) laser beam it is therefore very easy to get a rough idea of the slope of the gradient. This method is particularly useful for very steep gradients where it becomes difficult to measure samples interferometrically. This is the case for the present samples produced using crystal growing techniques. Due to the steep gradients which have produced, it has been impossible to measure them interferometrically.

The infrared interferometer which has been set up is of the Mach-Zehnder type, using germanium beam splitters and piezo-electric modulator to allow A.C. operation. It was determined in usage that a mirror mounted on a permanent magnet speaker-like modulator was not stable enough to result in a useful interferometer. The largest problem here was that one could not maintain sufficient angular stability to allow for useful spatial resolution of
Figure 7. Gradient Sample IR3.
phase. This problem becomes even more severe when one tries to measure high spatial density fringes or equivalent steep gradient. Figure 8 illustrates the basic layout of the interferometer.

As an illustration of the resultant electrical signals received from the detector, the following pictures illustrate the effect of the electrical signal as the optical path of one arm of the interferometer is changed. This change in optical path is the quantity of interest as a scan is made with the detector across the sample. The upper waveform is the applied voltage across the piezo-electric modulator. The signal below it is the actual detected signal when the system is operated with a chopper in the beam. This is necessary because of the use of pyroelectric detectors which cannot detect d.c. intensity changes and subsequently requires modulation of the laser beam along with the modulation of the phase in the interferometer which is at a much lower frequency (~10Hz). It is easy to see the way in which the phase of the detected signal change relative to the phase of the modulation; this is a direct measurement of the optical phase (See Fig. 9).

One of the limiting aspects of this system is the fact that as it is currently being operated the A.C. phase modulation is less than 2π. This limitation arises from the use of the piezo-electric modulator. Some of the advantages of >2π modulation are: it becomes much easier to correct for nonlinearities in the modulating system, it becomes much simpler electronically to accurately measure the electrical phase, and the system as a whole is much more stable. It is therefore advantageous to try and increase the modulation so that one is working in this domain.

The other limiting aspect of using an interferometer for measurement of gradient materials arises from the fact that steep gradients cause large beam deviations and it becomes difficult to measure the gradient accurately if at all. It is difficult to image and subsequently resolve the fringe pattern formed by the sample at the detector. This problem is more pronounced in the infrared because of the large wavelengths involved, and from the point of view of diffraction one is forced to use very low f/# imaging systems. This is a problem because "fast" systems tend to require higher field angles to view a sample and subsequently increases in aberrations.

As things stand now, interferometry has been the least useful tool for the measurement of infrared gradients. The reasons for this are all based on system limitations, and the need for improvements. Interferometry is the only real hope for characterizing gradients to the extent necessary for the accurate testing of gradients. Therefore, more work should be done to improve the system. The other two techniques which were discussed are useful for the preliminary measurement of materials but cannot give anywhere near the resolution needed to produce accurate enough information to allow for the use of infrared gradient materials in optical systems.

III. Ray Tracing in Anamorphic Gradient Index Media

There are a number of optical systems in which the power or magnification in one principal meridian is different from that of the other meridian. In conventional systems this effect is achieved by the use of components that have cylindrical surfaces. The performance of these anamorphic systems is limited by the difficulties associated with fabricating cylindrical surfaces to within close tolerances.
Figure 8. Infrared A. C. Interferometer.
The incorporation of gradient index components into rotationally symmetric systems has proven to be a useful design technique. A complicated series of homogeneous lenses may often be replaced by a smaller number of gradient index lenses. The additional degrees of freedom associated with the profile of the gradient make it possible to match or improve upon the performance of the homogeneous system. Similarly, it is expected that non-rotationally symmetric gradient index components could be used advantageously in the design of anamorphic systems. For the analysis and design of such systems, the designer needs to be able to predict the paths of rays through non-rotationally symmetric gradient media that may have spherical surfaces.

If a Cartesian coordinate system is chosen, the path of a ray through a general index medium is described by two coupled second-order differential equations:

\[
\frac{\partial N}{\partial x} \frac{\mathrm{d} Y}{\mathrm{d} x} + \frac{\partial N}{\partial y} \frac{\mathrm{d} Y}{\mathrm{d} y}(1 + \frac{\mathrm{d} Y}{\mathrm{d} x} \frac{\mathrm{d} Z}{\mathrm{d} y} + \frac{\mathrm{d} Z}{\mathrm{d} y}) + N Y = 0
\]

\[
\frac{\partial N}{\partial x} \frac{\mathrm{d} Z}{\mathrm{d} x} + \frac{\partial N}{\partial z} \frac{\mathrm{d} Z}{\mathrm{d} z}(1 + \frac{\mathrm{d} Z}{\mathrm{d} x} \frac{\mathrm{d} Y}{\mathrm{d} z} + \frac{\mathrm{d} Y}{\mathrm{d} z}) + N Z = 0
\]

(6)

These are the result of the application of the Euler equations to Fermat's principle. Since these equations cannot be solved in general, some restrictions must be placed on the representation of the ray path and the index profile. The ray path is expanded in two power series in \( x \), the coordinate along the optical axis:

\[
Y(x) = \sum_{j=1}^{\infty} A_j x^{j-1}
\]

\[
Z(x) = \sum_{j=1}^{\infty} B_j x^{j-1}
\]

(7)

The coefficients \( A_j \) and \( B_j \) give the position of the ray as it enters the medium, and \( A_2 \) and \( B_2 \) give the direction of the ray.

The index distribution is expanded in a double power series:

\[
N(x, c_n) = \sum_{n=0}^{N} \sum_{m=0}^{M} N_{nm} x^n z^m c_n^n
\]

where

\[
c_n = a_n y^2 + b_n z^2 + c_n x^2 + 2d_n y z + 2e_n y x + 2f_n z x +
\]

\[
g_n y + h_n z + i_n x + k_n.
\]

(8)

The radial component \( c_n \) represents media in which the surfaces of constant index are ellipsoids. The coefficients \( a_n \), \( b_n \), and \( c_n \) give the shape of the ellipsoid, \( d_n \), \( e_n \), and \( f_n \) allow rotations about the coordinate axes, and \( g_n \), \( h_n \), \( i_n \), and \( k_n \) give the decentration of the ellipsoids with respect to the coordinate system. In the case of an anamorphic lens, \( c_n = 0 \), that is, the width of the ellipsoid is infinite in the direction of the optical axis.
Figure 9. Direct Measurement of the Optical Phase.
With these expansions for the ray path and the index distribution, the differential equations can be solved. If the initial height and slope of the ray are known and the coefficients \( N_{nn} \) are given, then \( A_3, A_4 \ldots \) and \( B_3, B_4 \ldots \) need to be calculated.

To simplify the solution of the differential equations, each term is expanded in a separate power series:

\[
1 + y^2 + z^2 = \sum_{j=1}^{\infty} H j^{j-1},
\]

(9)

\[
\delta N = \sum_{j=1}^{\infty} G j^{j-1},
\]

(10)

\[
\delta x = \sum_{j=1}^{\infty} E j^{j-1},
\]

(11)

\[
\delta N = \sum_{j=1}^{\infty} F j^{j-1}
\]

(12)

\[
N = \sum_{j=1}^{\infty} D j^{j-1}
\]

(13)

When these expansions are introduced into the differential equations, two recursion relations result:

\[
A_{k+2} = -\frac{1}{k(k+1)D_1} \sum_{m=1}^{k} m A_{m+1} \sum_{n=1}^{k+1-m} G_{k+2-m-n} H_n
\]

(14)

\[
- \sum_{m=1}^{k} E_m H_{k+1-m} + \sum_{m=1}^{k-1} m(m+1) A_{m+2} D_{k+1-m}
\]

and

\[
B_{k+2} = -\frac{1}{k(k+1)D_1} \sum_{m=1}^{k} m B_{m+1} \sum_{n=1}^{k+1-m} G_{k+2-m-n} H_n
\]

(15)

- \sum_{m=1}^{k} F_m H_{k+1-m} + \sum_{m=1}^{k-1} m(m+1) B_{m+2} D_{k+1-m}

Next, equations are derived for the coefficients \( H_j, G_j, E_j, F_j, \) and \( D_j \). From Eq. (9),

\[
H_j = \sum_{m=1}^{j} m(j+1-m)(A_{m+1} A_{j+2-m} + B_{m+1} B_{j+2-m})
\]
For the terms involving the index of refraction, an expansion for $\zeta_P$ is needed. If the power series for $\zeta_n$ is defined as

$$\zeta_n = \sum_{j=1}^C C_{n,1,j} x^{j-1}$$  \hspace{1cm} (16)

then

$$C_{n,1,j} = \sum_{m=1}^J \left( a_n A_{m} A_{j+1-m} + b_n B_{m} B_{j+1-m} + 2 d_n A_{m} B_{j+1-m} \right)$$

$$+ b_n A_{j} + h_n B_{j}$$

$$\{ + 2 e_n A_{j-1} + 2 f_n B_{j-1} \} \hspace{1cm} j>1$$

$$\{ + k_n \} \hspace{1cm} j=1$$

$$\{ + i_n \} \hspace{1cm} j=2$$

$$\{ + c_n \} \hspace{1cm} j=3$$  \hspace{1cm} (17)

For other powers of $\zeta_P$

$$\zeta_n = \sum_{j=1}^C n,p,j x^{j-1}$$  \hspace{1cm} (18)

and the coefficients $C_{n,p,j}$ can be expressed in terms of $C_{n,p-1,j}$ and $C_{n,1,j}$

$$C_{n,p,j} = \sum_{m=1}^J C_{n,1,m} C_{n,p-1,j+m}$$  \hspace{1cm} (19)

For $n = 0$ define $C_{0,p,j} = 1$. With these expansions, the expression for $N$ can be found. Using Eq. (13),

$$D_j = N_{0,j-1} + \sum_{n=1}^J \sum_{m=1}^n N_{n,m-1} C_{n,n,j-m+1}$$  \hspace{1cm} (20)

The derivation of the expressions for $E_j$, $F_j$ and $G_j$ requires two more definitions:

$$\sum_{j=1}^C a_{n,p,j} x^{j-1} = 2 \sum_{j=1}^C A_j x^{j-1} \sum_{j=1}^C C_{n,p,j} x^{j-1}$$

$$\sum_{j=1}^C b_{n,p,j} x^{j-1} = 2 \sum_{j=1}^C B_j x^{j-1} \sum_{j=1}^C C_{n,p,j} x^{j-1}$$  \hspace{1cm} (21)
Equating terms with equal powers in \( x \) gives

\[
C_a, n, p, j = 2 \sum_{m=1}^{j} C_{n, p, m, A_{j-m+1}}
\]

\[
C_b, n, p, j = 2 \sum_{m=1}^{j} C_{n, p, m, B_{j-m+1}}
\]

and for \( p = 0 \)

\[
C_a n, 0, j = 2 A_j
\]

\[
C_b n, 0, j = 2 B_j
\]

Then from Eq. (10), the coefficients of \( \frac{\partial N}{\partial x} \) can be expressed

\[
G_j = j N_{0j} + \sum_{n=1}^{j} \sum_{m=1}^{j} (m N_{nm} C_{n, j-m+1} + n N_{n, m-1} (c_n C_{a, n-1, j-m+1} + d_n C_{b, n-1, j-m+1}))
\]

\[
+ i_1 N_{1, j-1} + \sum_{n=2}^{j} \sum_{m=1}^{j-1} i_n n N_{n, m-1} C_{n-1, j-m+1}
\]

\[
\left( + 2 c_1 N_{1, j-2} + \sum_{n=2}^{j-1} \sum_{m=1}^{j-1} 2 c_n n N_{n, m-1} C_{n-1, j-m} \right)
\]

\[
= (j-1)
\]

and the derivations with respect to \( Y \) and \( Z \) are

\[
E_j = \sum_{n=1}^{j} \sum_{m=1}^{j} n N_{n, m-1} (a_n C_{a, n-1, j-m+1} + d_n C_{b, n-1, j-m+1})
\]

\[
+ g_1 N_{1, j-1} + \sum_{n=2}^{j} \sum_{m=1}^{j-1} g_n n N_{n, m-1} C_{n-1, j-m+1}
\]

\[
\left( + 2 e_1 N_{1, j-2} + \sum_{n=2}^{j-1} \sum_{m=1}^{j-1} 2 e_n n N_{n, m-1} C_{n-1, j-m} \right)
\]

\[
= (j-1)
\]
and

\[ F_j = \sum_{n=1}^{j} \sum_{m=1}^{j} n N_{n,m-1} (d_n C_{n,n-1,j-m+1} + b_n C_{b,n,n-1,j-m+1}) \]

\[ + h_i N_{i,j-1} + \sum_{n=2}^{j} \sum_{m=1}^{j} h_n n N_{n,m-1} C_{n,n-1,j-m+1} \]

\[ ( + 2 f_l N_{l,j-2} + \sum_{n=2}^{j-1} \sum_{m=1}^{j} 2 f_n n N_{n,m-1} C_{n,n-1,j-m} ) \]

Although the equations that have been described are complicated, they can be easily adapted to DO-loops in a computer program. The ray trace algorithm has been programmed and a series of spot diagrams have been generated. Rays were traced from an axial object point through an anamorphic Wood lens that has a tangential focal length of 20 and a sagittal focal length of 10. The third order spherical aberration has been corrected in each dimension with the coefficients \( N_{20,2} \), \( a_2 \), and \( b_2 \). The first three figures are spot diagrams at three different focal positions. Figure 10 shows the ray positions at the sagittal focal plane, Figure 11 was generated at the tangential focal plane, and Figure 12 gives the ray positions at a plane halfway in between. The line foci that are observed demonstrate the presence of axial astigmatism in an anamorphic lens.

The remaining series of figures are spot diagrams obtained by tracing rays through the same anamorphic Wood lens, but now the gradient has been rotated about the optical axis by 25°. As would be expected, Figure 13, 14, 15 show that the spots merely rotate by 25°.

The ray trace procedure that has been described allows the designer to compute the paths of rays in anamorphic gradient index media. The algorithm is fast and efficient enough to be incorporated into an automatic design program. The ray trace can then be used as an important analytical tool with which to evaluate the importance of anamorphic gradients in optical design.

IV. Fabrication of Six Gradient Index Samples

The six lenses were produced by exchanging ions of a conventional homogeneous glass with ions of the same valence from a molten salt. The sample is cylindrical with a diameter of 1.25 cm and a length of 3.75 cm. The base glass, manufactured by Bausch and Lomb, is an alumino-silicate glass containing approximately twenty-five weight percent sodium and no other valence one ions. Lithium bromide salt (melting point = 550°C) is used as the diffusant. The following table summarizes the fabrication procedure:

<table>
<thead>
<tr>
<th>Time (Hours)</th>
<th>Process Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>ramp temperature from 20°C to 200°C (Oven rate)</td>
</tr>
<tr>
<td>34.40</td>
<td>ramp temperature from 200°C to 572°C</td>
</tr>
</tbody>
</table>
Sample Timetable (Continued)

<table>
<thead>
<tr>
<th>Time (Hours)</th>
<th>Process Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>36.33</td>
<td>ion exchange at 572°C</td>
</tr>
<tr>
<td>29.33</td>
<td>post heat treatment in air at 546°C</td>
</tr>
<tr>
<td>33.50</td>
<td>ramp temperature 546°C to 200°C</td>
</tr>
<tr>
<td>24.00</td>
<td>ramp temperature 200°C to 20°C (Over rate)</td>
</tr>
</tbody>
</table>

The sample was removed from the salt and post heat treated to eliminate the stress induced by contraction of the salt as it resolidifies. The temperature chosen for the post heat treatment is below the melting point of the salt. This allows the salt to resolidify and reduces the amount of vapor in the oven.

The oven specifications are as follows:

- **control**: Lindberg 1000 controller specifically designed for temperature control to an accuracy of better than ±10°C
- **setability**: 1°C
- **accuracy**: typically ±1°C maximum with a change of ±5°C ambient temperature
- **stability**: maximum ±1°C over a one week period
- **compensation**: maximum ±0.5°C with a ±10% change in line voltage

The lenses were fabricated by cutting plane-parallel slabs from the cylindrical samples and polishing the faces. The actual index profile was measured using an a.c. Mach Zehnder interferometer. The results are given in the accompanying Figure 16. It can be seen that there is a change in the index of refraction of 0.013 from the center to the edge of the sample. The index is higher at the edge of the sample than it is at the center. The index profile at $\lambda = 0.5145 \mu m$ is described by

$$\Delta n = 1.5062 + 0.00112 r^2 - 0.0000296 r^4$$

In the lens with a thickness of 3mm, this corresponds to a focal length of -148.5 mm.

V. Technology Assessment

The technology assessment of gradient index optics can be divided in a number of different ways. The first choice would be to do the division by design, materials, testing, and manufacturing capability. An alternative method is to perform the assessment by geographical area, i.e. by country or by company. In this report we have chosen the former approach. In all cases,
Figure 10. Focal distance = 9.37.
Figure 11. Focal distance = 14.37.
Figure 12. Focal distance = 19.37.
Figure 13. Focal distance = 9.37.
Figure 14. Focal distance = 14.37.
Figure 15. Focal distance = 19.37.
Figure 16.
however, we have tried to assess each company's and country's capabilities. This is particularly important since the gradient index technology is divided among two major groups; the group in the United States and that in Japan. The effort in Japan is much more solidified and organized, while the work in the United States is very highly fragmented without interaction of the others.

This section of the report is divided into four major areas: (1) The design of optical systems using gradient index, (2) the manufacture of materials, (3) the measurement of the properties of materials, and (4) production methods. In all cases, the current technology has been discussed, and the areas of future research and development are explored.

A. Design of Gradient Index Systems

One would believe that a large amount of design effort would have been performed in order to determine what types of profiles would be suitable for gradient index systems. This, in fact, is not the case. One method of determining the measure of the design is the number of patents issued in the gradient index field. At this writing, only two design patents have been issued [30, 31]. While other patents allude to certain design profiles, particularly the parabolic profile, complete design analysis has never been completed. Further, tolerance analysis on the profiles and on the systems themselves has not been conducted for either of the patented systems. The difficulty in the design analysis is principally due to the complex formulae that are involved and in calculating a third and higher order aberration coefficient of these systems. Ray-trace analysis has been used, but most algorithms are based on the integral solution of the ray-trace equations which are very time consuming and costly even on the fastest computers. These problems have been solved, and it is now possible to analyze gradient index systems. However, computer lens design programs involving gradient index systems are not available. For example, the major programs in the United States (CODE V, ACCOS V, COOLGENT) do not have the capability of analyzing gradient index systems. The exception is the CODE V program which will allow the analysis of very weak gradients introduced by thermal variations in optical components. The only program in the United States that has such capability is the program at the University of Rochester (ADIOS). While this program has been available under various circumstances to people outside of the University of Rochester, the requests for such use have not been overwhelming. The lens design community is by in large very conservative and is waiting for the materials to be developed. Therefore, until more materials are available, it will be difficult to convince lens designers to even consider these types of systems.

The other major effort in design revolves around the so-called Selfoc or grinrod. In these types of lenses, the profile is parabolic or nearly parabolic in the radial coordinate. The diameters of these lenses range from 1 to 5 mm, hence they are called rod lenses. These designs are principally being conducted by researches in Japan at Nippon Sheet Glass. The diameter of these rods limits their application and in general are not applicable to conventional lens systems. However, when a series of these rods are put together it is possible to create arrays of images. Arrays of Selfoc lenses have been used in photocopying lenses. (Current production of these arrays is approximately 30 thousand units per month. The cost of the systems is approximately $35 to $40 per unit. The only manufacturer of these systems is Nippon Sheet Glass of Japan). Other smaller efforts on design of systems are occurring at
Canon and Asahi Optical in Japan. The principal interest at these two facilities is the production of larger radial gradient lenses for photographic use. During my recent visit to Japan, I talked to a number of designers there who are doing gradient index design using radial gradients. Their capability is such that within 3 to 5 years, Canon or Pentax (Asahi) will probably have a commercial product embodying a gradient index system. The first application will probably be in lenses for the 110 format camera with subsequent applications for the 35 mm format. The level of effort in Japan is fairly high involving perhaps 2 to 3 designers in each of these two companies. I expect the other major camera companies, (Nikon, Minolta, Olympus) to be involved in this gradient index lens design. Their aggressive nature in this business seems to be outstripping that of the United States.

Miscellaneous designer efforts are occurring in the medical field, principally for the use of instruments and the endoscope systems. In the United States that effort is being carried out by Dyonics, a company in the Massachusetts area, and on a limited basis at American Cystoscope Makers, of Stanford, Connecticut. It has also been rumored that Olympus (Japan) has developed an endoscope with such materials. In all cases, the efforts are being limited by the choice of materials available to them. No effort has been made to integrate the materials and design aspects. The approach seems to be to accept whatever materials are being made by the Japanese and to design around them.

Another effort is being conducted by General Dynamics in the use of transmission of images on gradient index rods with distances of 1 to 3 meters. In this case, the infrared image is relayed to a remote sensor. It has been found that it is possible to transmit 100 by 100 data points over distances of 1 meter with a fiber that is only 4 mm in diameter if the image is at a wavelength of 10.6 microns. If the image is at visible wavelengths, then the fiber is reduced to less than 1 mm [32].

Other efforts are being conducted at very low levels including the use of gradient index for video disk applications, microscope objectives and for a non-unit magnification copying lens.

Very few people have been willing to make the effort to design highly sophisticated lenses without any knowledge of the materials properties that are possible. The approach at the University of Rochester has been to design lenses without regard to the profiles that are needed and to establish goals for the materials manufacturers. Over the last few years, a number of design studies have been conducted which have resulted in lenses of the following types: (1) A one element binocular objective to replace a four element system in the M-19 military binocular [33] (2) the design of a photographic objective for a 35 mm camera which will replace the six element Double Gauss system with a 2 element gradient index system [34] and (3) an analysis of the photocopying array system where the use of gradient index lenses was optimized [35]. Each system established the theoretical limit for the number of elements that can be eliminated. It is now the feeling of the group at Rochester that the conversion between gradient index systems and conventional systems is 3 to 1, i.e. if a lens system has 6 elements, this system can be reduced to 2 elements using radial gradient optics. The conversion to axial gradients is not quite so obvious, as it depends to a great degree on the type of aberrat-
tion present. If the lens is dominated by its axial performance, then axial gradients have an important influence on it. However, if the lens is dominated by chromatic aberrations or field curvature, the axial gradient is not effective.

The only way that gradient index systems will become a viable entity, is for some systems to be manufactured and demonstrated to the optics community showing that this is a viable technique. Currently, no company is willing to invest the development cost, which involves the design of a particular system and the manufacture of a number of prototype systems to determine that this is a viable technology. This seems to be limited by the amount of money that will be necessary in development costs (probably between 1 and 2 million dollars) and the nature of the business community which would require the payoff in a very short term.

B. Materials

The most important aspect of the gradient index optics is the materials research. As is the case in a developing technology, we are limited by materials research and the availability of suitable materials for optical components. This need is independent of the wavelength or the lens system. No matter what gradients are manufactured, the designer will always need larger index of refraction differences or greater depths of the gradients, thus putting severe restrictions on the types of lens systems that can be made. However, the current limitations are so restricted that it is impossible to make most gradient index lens systems in production. The exception is small radial gradients manufactured by the Japanese.

In order to adequately assess the technology in this area, it is necessary to describe in some small detail the techniques that are used and limitations in each of these techniques, including the maximum index change that can be produced, the depth of the gradient and the mechanical properties that are created by the gradient. The techniques that can be used to make gradient index materials (either glass, plastic or crystalline) are ion exchange, ion stuffing in phase separated glasses, chemical vapor disposition, vapor phase axial deposition, neutron radiation, ion bombardment, photopolymerization in either glasses and mixtures, and crystal growth.

1. Techniques for Manufacture of Gradients

The simplest technique for making a gradient in a glassy material is ion exchange. In this method, one ion from a glass is exchanged for an ion in a bath. The bath is normally a salt solution such as lithium bromide or silver chloride, raised to a temperature above its melting point but below the softening point of the glass. The thermal energy is sufficient to unbind the ion in the glass from the glass structure and the ion is exchanged for an ion in the bath. In the simplest form, this diffusion follows the same equations as does the gas law diffusion with time constants orders of magnitude slower. The depth of the gradient is determined by the length of time and temperature of the diffusion while the maximum index change is determined by the glass composition. For example, if there is a large number of ions that can be exchanged out of the glass for ions in the glass, large index of refraction changes can be created. Two effects determine the index of refraction change. The first is the difference of the polarizability of the ions themselves, and secondly and as important is the change in density of the glass.
For double valence ion such as lead, zinc, and cadmium the index change can be rather large; however, the binding energy of these ions in the glass structure is rather high and thus, the depth of the gradient that can be created is relatively small. As is the case with many types of materials research we are left with a trade-off between the maximum index change and the depth of the gradient. If more mobile ions (potassium, lithium, and sodium) are used, a very deep gradient can be formed, but the maximum index that can be created is of the order of 0.04. In recently completed research, the group at Grenoble, France has reported index changes of 0.22 by this technique [36]. The host glass TiF-6 manufactured by Schott Optical in Mainz, Germany, has a large concentration of lithium and potassium. By exchanging silver for this material, very large index gradients can be formed. However, the depth of such a gradient is limited to approximately 100 to 150 micrometers. Larger depths are not possible as the mechanical properties of the glass are changed considerably and the glass fractured with larger depth in creating. Again, a smaller gradient could be created over a larger depth. No unified theory has been developed at this point which described this phenomena, and thus it is impossible to give an exact relationship for the maximum index change versus depth of the gradient. This would provide a very interesting piece of research which would be conducted in the next three years.

Ion exchange is a simple technique to implement which requires only normal annealing ovens and a few days of time. No special instrumentation is required. The accuracy of the oven should be held to ± 0.5°C. It is therefore probable that ion exchange will remain a viable technique for manufacture of gradients for at least a decade until other techniques are sufficiently developed. The range of index changes and depth of gradients is sufficiently large (ΔN's of 0.22 or depths of up to 10 mm).

In Japan, the principle technique for making gradient index glass for imaging purposes is the ion exchange method. The glass that is used there is cesium based and potassium ions are exchanged from a potassium nitrate bath into the glass material. The resulting lens systems has considerable chromatic aberration. As a result of work done by Fantone and others, it has been found that in exchange for lithium for potassium, it makes much better achromatized systems. Therefore, it is expected by the end of this year, that they will be changing to a lithium based glass and exchanging either potassium or sodium into it. This will result in a slightly lower gradient, but will result in better chromatic correction.

The future areas of research for ion exchange include the unified theory of the index change and depth. In order to accomplish this task it is important to have a theory that predicts mechanical properties (variation of expansion coefficient and change of index with temperature). Research in this area is continuing. However, the problems of making such measurements to verify the theory are complicated. Once this is done however it will be possible to determine the maximum number of ions that can be exchanged before the glass will fracture. This will be an important addition to the index change and chromatic properties models. The most important development for ion exchange is to start the task of building a pilot project to determine what are the problems of actually producing these types of materials. While
the Japanese have already accomplished this in geometries of 1 to 5 mm., no such project has been undertaken in the United States. Of all the techniques described in this section this is the most viable one and the one that is closest to actual production.

2. Gradients in Plastics

There seem to be two different methods for introducing gradient index in plastics. The first is to mix two polymer materials together (see patent by Hamblen, No. 4,022,855.) The second is to use the photorefractive effect to partially polymerize the monomer. This technique can be divided into two subcategories. The first method uses ultraviolet light which is varied across the sample to introduce varying amounts of polymerization. The work on mixing of polymers was originally conducted at Eastman Kodak Company. This work has ceased, principally due to the difficulty of keeping uniformity of the gradient within the volume. The very nature of the mixing process made it very complicated and it was not possible to introduce arbitrary gradient profiles.

In the second technique the absorption energy of two intersecting laser beams is used to partial polymerize the material. In the intersection volume of the two laser beams, there is sufficient energy to introduce this photorefractive effect. (see patent by Swainsen, No. 4,041,476) The work on this effect has been rather limited.

Work on ultraviolet setting plastics has been investigated as a permanent recording material for video disk or optical disk memories. In this application, both read-write and read-only memory have been explored. The plastics have inherent problems for this application, but the results of some of this research may be applicable to gradients. Perhaps the most interesting technique is that of two photon absorption using two laser beams. At least in principle it should be possible to write arbitrary gradient profiles within the volume, thus making very complicated gradients that would not otherwise be possible. At this writing, only Battelle in Columbus, Ohio, has done any work on this process, and that work has been rather limited. This is probably the most exciting way of making gradients because of its potential for arbitrary profiles. Further, the possibilities of reducing the thermal problems in plastics may be possible with these materials as these thermal effects from the gradient may counteract those from the normal plastic materials. At this writing, no such measurements have been conducted. Further, no materials model exists currently to predict the gradient, its spectral properties or its mechanical properties. This appears to be very important area for future gradient index research. Parenthetically it should be added, however, that the use of plastics in Army systems may not ever come to be. The very nature of the softness of the materials, their thermal properties, may not be correctable from gradient materials. However, it is worth at least a small investigation to determine the possible mechanical thermal properties. I am not, however, very hopeful that they will be applicable to normally fielded army system.

Another effort in plastics is being conducted in Japan by the group at Keio University. Their work has been continuing for over ten years now and the lenses that I have seen are very good. Their technique is to simply use ultraviolet light to create the gradient. Similar research is going on at
Tokyo Institute of Technology and the University of Tokyo. It is clear from my recent visit to Japan, that they are perhaps two to five years ahead of us in the research in this area.

3. Deposition Techniques

There are two methods of depositing glassy materials which have been used to create gradient index glasses. The older technique called chemical vapor deposition (modified chemical vapor deposition), CVD, has been used for making low loss gradient index and step fibers for a number of years. In making a gradient index fiber, a series of layers of homogeneous glass are deposited on the inside of a tube material. (The technique can also be used on the outside of the tube and is called outside CVD). Each composition of glass that is deposited has a slightly different composition than its neighbor. By varying the composition of the materials, the index of refraction can be varied in a prescribed way. In optical communications, the index profile is normally parabolic. This material which is approximately 25 mm. in diameter is then drawn down to a 50 micron gradient index fiber. The layers which were tens of micrometers thick originally are now less than the wavelength of light after drawing. Thus, the gradient is continuous to the optical radiation. To modify this technique for fabricating large geometry optics requires many more layers of glass. In order to make the glass look continuous, it would be required to increase the number of layers by a factor of one hundred. In doing so, the time of fabrication would be substantially increased. Further, the cost of the material that is used in optical communications is rather high. This creates an additional problem for commercialization.

On the more positive note, it would be possible to use CVD with less expensive materials. The cost of the materials in optical communications is dictated by low losses that are required over tenths of kilometers. This is not a requirement in imaging optics, and thus less pure and presumably less expensive materials could be used. While there are a number of difficulties in trying to do this with other materials, this does not rule out this as a possible technique.

The second technique for deposition of glass is called vapor phase axial deposition (VAD). This technique was developed by Nippon Telephone and Telegraph in Japan. In this case, material is again deposited in a way somewhat similar to the CVD process, except that it is done in an axial manner, (that is along the optical axis of the element). By varying the temperature radially, the gradient can be made continuous from center to edge and glasses of arbitrary length can be manufactured. However, this method also suffers from the cost of materials and deposition rates. The time required to make reasonable sized elements may be several hundred hours. The advantage of continuous gradients make it possible to fabricate two inch diameter optics. This has been successfully completed in Japan; however, the use for optical lenses has not been demonstrated yet.

In the same way as CVD process is used for the making of glasses it can also be used for manufacturing other materials. For example, the technique of using CVD for making zinc selenide and zinc sulfide has been used for many years at Raytheon Corporation. By coevaporating the materials and varying the composition, it is possible to create an index gradient. Zinc
Selenide has an index of 2.4 and zinc sulfide has an index of 2.2, thus with very small changes in composition very large index variations can be created. This has actually been completed for a very different purpose - to increase in the mechanical stability of zinc selenide. As is well known, the zinc selenide does not perform very well in hostile environments, while the zinc sulfide does. However, the zinc sulfide does not have the high transmission that zinc selenide possesses. Therefore, in order to increase the atmospheric durability of zinc selenide, the two materials are coevaporated near the outer boundary to strengthen it. This creates a slight gradient which is impermeable. However, the fact that this has already been accomplished by Raytheon indicates that this is a viable technique for making infrared transmitting gradients.

4. Miscellaneous Techniques

A number of techniques have been proposed over the years to produce gradient index materials. These techniques include phase separated glasses and ion or molecular stuffing, neutron irradiation, ion bombardment, and crystal growth. In the first technique, a glass is made to phase separation by heating [37]. One of the phases is dissolved in an acid bath and a glass matrix (sponge) remains. The sponge can then be stuffed with various molecules or ions to create a variation in the index of refraction. The structure is very loose, and it is possible to diffuse ions to a very large depth. In principle, this should be a very good technique; however, it suffers from the problem that most glasses do not phase separate uniformly on the submicrometer level. Variations in phase separation cause variations in stuffing, which cause local variations of the gradient. These are not acceptable because they cause high frequency variation of the gradient. Some work has been conducted on this technique at Catholic University and at Battelle Labs, of Columbus, Ohio. The principle emphasis has been to get more uniformly phase separated glasses by using the Sol-Gel process. This technique forms the glass from liquids rather than from solids. The underlying theme is that liquids mix more uniformly, and thus if the glass is formed from these it would be more uniform. When the phase separation is conducted it also will be uniform. Work is continuing on this problem, but this will not be a viable technique until uniformly phase separated glasses are available.

Neutron irradiation has been proposed [38]. In this technique, the boron changes state by absorbing the neutron and thus changes its index of refraction. This technique has been used in France on a limited basis, but the technique causes the glass to yellow and makes the glasses radiation hot for a period of time. The depths of the gradients are limited to less than one millimeter. This does not appear to be a viable technique for gradient index.

Ion bombardment is a variation of a neutron irradiation technique. Here, ions are bombarded onto the surface to cause an index of refraction in gradients. In this case, the depths of the gradients are even less than the previous one being limited to less than one hundred microns in depth.

Gradient index crystals can be grown. In this technique, a seed of one material is used to pull a crystal from a bath of material which has two or more constituent parts. Depending upon the nature of the crystal growing process, one of the parts of the bath will be preferentially drawn out of it.
onto the crystal plane. In the case of germanium and silicon the higher segregation coefficient of silicon creates an index of refraction gradient of silicon down the crystal. This has been previously reported in the other section of this report. In addition, gradient index crystals of sodium chloride and silver chloride have also been manufactured. This of course creates very unique crystals, the profile being determined by the concentration variation and the growth rate. It is certainly an interesting approach for making infrared transmitting materials.

C. Measurements

The invention of gradient index materials has created some interesting problems for characterization. It is necessary to measure the index of refraction as a function of spatial coordinate, and its dependence on wavelength and temperature. In addition, most models predicting the index of refraction are based on compositional data; therefore, ion probe or some other technique for measuring the materials aspects of the materials are necessary. Standard techniques of ion probe have been used and appear to be satisfactory. Other techniques of x-ray diffraction of ESCA and EDAX are also possible. In general, it is necessary to measure concentrations to approximately 1/10 of a percent by weight with a lateral resolution of 10 to 15 micrometers.

The optical measurements are fairly straightforward also, although they require a great deal of expensive instrumentation. The use of interferometry, imaging techniques, schlieren system, moire fringe topography, and autocollimation have been reported in literature. For reference to complete measurement techniques, the reader is referred to reference number 39.

The only remaining problems in measurement rest on making measurements at an unusual wavelength (non visible) and making the measurement of the thermal and mechanical properties of gradient index materials. Since there is a variation of chemical composition with the glass, we expect a variation of thermal expansion coefficient dn/dT. No instrument currently exists for this measurement and it will be a very important one before these systems are fielded. One of the important implications may be the ability to athermalize single element lenses. This would create a very important step to making environmentally insensitive optical systems. Other measurements that may be important are those of stress at the surfaces. It would be possible to put the surface layers under compressive stress so that the surfaces are harder than they normally would be. This is exactly the technique that is used in chemical strengthening of glassy materials. No techniques currently exist for these measurements.

Generally the problems of measurements are well under control and within one to four years most of the problems currently stated should be solved.

D. Production Capability

Currently only one facility exists in the world for the production of gradient index components. This factory located in Sagamihara, Japan produces the photocopying arrays from a series of gradient index rods. These rods are approximately 1 mm. in diameter and are 25 mm. in length. A photocopying array comprises approximately 600 of these rods in two linear rows. Currently
this facility is producing between 20 and 30 thousand units per month, although the estimated capability of this factory is approximately 60 units per month. These arrays are used exclusively in Japanese manufactured copying machines, although it is expected that within a year that a U. S. manufacturer will also be using these same systems. The philosophy of Nippon Sheet Glass has been not to second source these, but rather to keep 100% of the production in Japan. While they are aware of the difficulties of this from the U. S. purchasing standpoint, they seem unwilling to license. While other facilities exist for the high production of low loss optical communication fiber by the chemical deposition and other deposition techniques, these techniques do not lend themselves to the production of large diameter gradients. Further, no development has been done on the various materials (described in an earlier section) to establish the difficulties of actually producing gradients in large volumes over geometries needed for normal lenses. The problems of production are not unique to the visible, but extend to the infrared as well. It is expected that in order to adequately manufacture gradients in either visible or infrared, a development between 1 and 2 million dollars will be necessary. This can only be an estimate as the exact technique that will be used to manufacture gradients has not been established. This estimate is based on an ion exchange process.

Perhaps the most significant contribution that can be made to gradient index is to create an environment in which these techniques can be developed. Cross-fertilization of the academic, industrial, and governmental communities is needed to create a gradient index optical industry.
REFERENCES


8. D. T. Moore, Adios, Computer lens design program, University of Rochester.

9. G. W. Johnson, Iglo, Computer lens design program, University of Rochester.


REFERENCES


REFERENCES


## DISTRIBUTION

<table>
<thead>
<tr>
<th>Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIT Research Institute</td>
</tr>
<tr>
<td>ATTN: CACIAC</td>
</tr>
<tr>
<td>10 West 35th Street</td>
</tr>
<tr>
<td>Chicago, Illinois 60616</td>
</tr>
<tr>
<td>DRSMI-LP, Mr. Voight</td>
</tr>
<tr>
<td>DRSMI-X</td>
</tr>
<tr>
<td>DRSMI-R, Dr. McCorkle</td>
</tr>
<tr>
<td>-RG</td>
</tr>
<tr>
<td>-RGC</td>
</tr>
<tr>
<td>-RGT</td>
</tr>
<tr>
<td>-REO</td>
</tr>
<tr>
<td>-REI</td>
</tr>
<tr>
<td>-RE</td>
</tr>
<tr>
<td>-RR, Dr. Hartman</td>
</tr>
<tr>
<td>-RR, Dr. Guenther</td>
</tr>
<tr>
<td>-RR, Dr. Gamble</td>
</tr>
<tr>
<td>-RN, Dr. E. Dobbins</td>
</tr>
<tr>
<td>-RPR</td>
</tr>
<tr>
<td>-RPT Record Copy</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No. of Copies</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>15</td>
</tr>
<tr>
<td>1</td>
</tr>
</tbody>
</table>