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CHARACTERIZATION OF INFRARED OPTICAL PROPERTIES OF
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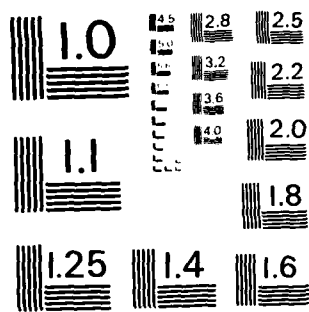
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Chemical and structural imperfections which occur in highly transparent insulators and semiconductors were studied by a range of electromagnetic and electronic techniques. These utilized infrared wavelength modulation, high contrast Raman and Brillouin scattering and photoinduced transients spectroscopy techniques. The spectral distribution of the absorption in the spectral region from 2.5-12 μm was measured by infrared wavelength modulation techniques on: CaF_2 , LiF , NaCl , NaF , LaF_3 , BaF_2 , MgF_2 , SrF_2 , MgO , KCl , and KBr . Both surface and volume contaminants were identified. The sensitivity of this technique were	

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19. CaF_2 , LiF , NaCl , NaF , LaF_3 , BaF_2 , MgF_2 , SrF_2 , MgO , KCl , KBr ; Si ; GaAs ; $\beta^{\text{I}}\text{-Cu}_x\text{Zn}_{1-x}$, $\beta^{\text{I}}\text{-AuZn}$, and $\text{Ag}_{0.7}\text{Zn}_{0.3}$.

20. at levels of 10^{-5}cm^{-1} . Rayleigh-Brillouin scattering was measured on single and polycrystalline KCl . In addition, Rayleigh-Brillouin and Raman scattering measurements were performed on fluoride glasses. The dispersion curves of the surface plasmas of n^{I} and Cu were measured by prism-coupler techniques. It was demonstrated that infrared wavelength modulation absorption can detect deep level impurity concentrations at levels of $10^{12}\text{-}10^{14}/\text{cm}^3$ in semiconductors. A detailed study was completed of the derivative absorption spectrum of GaAs:Cr revealed extensive fine structure which was correlated with a proposed energy level scheme of $(\text{Cr}^{3+}\text{-Cr}^{2+})$ ions in GaAs and indicated that a comparable number of Cr ions are at tetragonal and trigonal sites. Photoinduced transients spectroscopy revealed a number of deep levels in semi-insulating GaAs which are characteristic of the method of crystal synthesis. Wavelength modulated reflectivity measurements was used to study order-disorder effects on the band structure of $\beta^{\text{I}}\text{-Cu}_x\text{Zn}_{1-x}$, $\beta^{\text{I}}\text{-AuZn}$, and $\text{Ag}_{0.7}\text{Zn}_{0.3}$.

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Characterization of Infrared Optical Properties
of Transparent Materials

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A. OBJECTIVES OF PROGRAM

The broad objectives of this research program were to further our understanding of the intrinsic and extrinsic properties of highly transparent solids in the infrared region of the spectrum. The initial phases were directed towards the study of materials of relevance to infrared laser components. The later phase was concerned with semiconductor materials of interest to the electrical properties of layered semiconductors for low noise amplification, generation, and detection of high frequency radiation. The identification of chemical and structural imperfections which occurs in highly transparent insulators and semiconductors was studied by a range of electromagnetic and electronic techniques to analyze materials prepared by various material synthesis techniques. These utilize infrared wavelength modulation, high contrast Raman and Brillouin scattering, and photoinduced transients spectroscopy techniques.

The specific areas of research activity were:

Wavelength Modulation Spectroscopy of Insulators.

Scattering Losses in Single and Polycrystalline Materials for IR Fiber Applications.

Infrared Transparent Glasses Derived from the Fluorides of Hafnium, Thorium, and Barium.

Optical Measurements of Surface Plasmas in n^+ Si and Cu.

Deep Level Derivative Spectroscopy in Semiconductors.

Determination of Homogeneity of Doping, Alloy Composition, and Strain in Layered Semiconductors.

Oxygen in Floating Silicon.

Fully Electronic Servo Circuitry for Wavelength Modulation Spectroscopy.

De-Correlation Technique for Separation of Drude Parameters from Wavelength
Modulation Spectroscopy Data.

Photoinduced Transients Spectroscopy.

Light Scattering From Semiconductors.

Optical Properties of Metals.

B. SUMMARY OF THE STATUS OF THE RESEARCH.

The following are the problems studied and the summary of the conclusions reached. The reference numbers after each topic are to the publications referenced in the Publication List.

1. Infrared Wavelength Modulation Spectroscopy of Insulators [1,4]

The infrared wavelength modulation spectrometer system that we have developed has enabled us to perform unique measurements on highly transparent solids at levels of absorption of 10^{-5} cm. These techniques were employed on KBr and KCl and extended to other crystalline systems which are of interest in light guiding applications. A detailed study has been completed for KCl, KBr, CaF_2 , LiF, NaCl, NaF, LaF_3 , BaF_2 , MgF_2 , SrF_2 , and MgO. We have measured the continuous spectral distribution of the absorption in these materials in the spectral region from 2.5 to 12.0 μm . Previously, only measurements at discrete wavelengths by thermocouple laser calorimetry and photo-acoustic calorimetry were available. Rich and varied adsorption structures were observed in all these crystals, which enable us to identify volume and surface absorption. It is interesting to note that despite the diverse chemistry of these substances and the varied crystal growth techniques employed in the preparation of these materials, similar dominant bands are observed in most samples which are due to physisorption, volume, and surface chemisorption. However, the various fine structures observed in different crystals are indicative of the individual characteristics of the chemistry of the crystal preparation. These measurements which were performed in the laboratory and dry N_2 ambient readily show the physisorption and desorption of surface contaminants and allow the identification of the type of bonding of the particular constituents present.

The surface character of some of the absorption at levels of 10^{-4} to 10^{-5} cm^{-1} indicates the importance of performing measurements in the same ambient when comparing low level absorption measurements by various sensitive techniques.

The sensitivity of the infrared modulation techniques indicates that a fraction of a monolayer of surface adsorbed species can be detected. Experiments in controlled ambients on well characterized substrates using this technique can be rewarding for the physics and chemistry of surfaces.

The successful use of our infrared optical derivative system in the study of bulk and surface impurities in insulators at levels of 10^{-5} cm indicates that much remains to be done in the area of laser windows. It is clear that our λ -modulation measurements should be used in conjunction with a systematic study with crystal synthesis groups.

We have demonstrated that λ -modulation can be used to study deep levels at levels of sensitivity formerly only obtainable using DLTS electric measurements. In addition, we have shown that thin surface oxides can be studied by λ -modulation and optical scattering techniques. These studies are discussed in later sections of this report.

2. Scattering Losses in Single and Polycrystalline Materials for Infrared Fiber Applications [3].

There is a continuing technological interest to look for candidate materials which exhibit low optical losses at specific wavelengths for utilization in fiber optics and light guiding applications. Considerations have been given to the ultimate theoretical intrinsic-loss mechanisms and the practical extrinsic losses due to impurities and imperfections in crystalline and glassy materials. The ultimate transparency in materials should lie in a valley between the intrinsic electronic absorption edge and the tail of the

multi-phonon transitions. In this region, the ultimate losses should be due to Rayleigh and Brillouin scattering. The Brillouin scattering results from light that has been inelastically scattered (Bragg scattering) from acoustical phonons and is an intrinsic property of a given material. The Rayleigh scattering of light results from nonpropagating fluctuations in the dielectric constant. In glasses these fluctuations include: density variations resulting from frozen-in random variations in the dielectric in a disordered solid; concentration fluctuations resulting from local composition variations present in mixtures; entropy fluctuations resulting from temperature variations.

Polycrystalline KRS-5 and KCl are employed for fiber waveguides. Using our Rayleigh-Brillouin scattering system, we have completed an initial study of scattering from single and polycrystalline materials in cooperation with a group at the Hughes Research Laboratory to probe the mechanisms responsible for light scattering losses in highly transparent materials. Although we have found that polycrystalline materials scatter more strongly than single crystal materials, but have not as yet explicitly associated a particular elastic scattering process which contributes to the total scattering. Grain boundaries, dislocations, and the decoration of these structures by impurity-pinning and possible candidates. In addition, our results indicate that even in very pure single crystal KCl samples, there is more scattering than predicted for an ideal KCl crystal.

3. Fluoride Glasses [2,5].

The search for materials which exhibit low optical losses has been directed progressively to longer wavelength for the following criterion. Consideration of the various contributions to intrinsic scattering indicates that the minimum optical loss should occur at the intersection of the Rayleigh scattering curve

on the high frequency end and at the multiphonon edge at low frequency. Since the Rayleigh scattering losses exhibit a λ^{-4} wavelength dependence, it is clear that it is desirable to operate at longer wavelengths.

It has recently been discovered that it is possible to prepare a series of non-oxide glasses based on a mixture of ZF_4 and HfF_4 with other metallic fluorides. In the conventional preparation of these glasses residual impurities such as OH^- and $O^{=}$ can contribute extrinsic absorption and scattering centers. Because of our programmatic interest in highly transparent materials, we have turned our attention to the fabrication and optical measurements on these glasses. In collaboration with a group at the Hughes Research Laboratory, glasses consisting solely of high purity ZnF_4 , ThF_4 , and BaF_2 have been synthesized using reactive atmosphere processing (RAP) techniques. The utilization of RAP in the synthesis of these glasses has shown that infrared transparency and the mechanical strength of these halide glasses are greatly improved by eliminating anionic impurities such as OH^- and $O^{=}$ resulting in glasses which are continuously transparent from 0.3 to 7 μm and are water insoluble and unusually strong and hard.

In order to evaluate the scattering losses in these glasses, Rayleigh-Brillouin and Raman measurements were performed. By measuring the ratio of the intensity of the Rayleigh to Brillouin scattered light - the so-called Landau-Placzek ratio, one can obtain the attenuation due to scattering in terms of calculable scattering losses. Such measurements were performed on two glass systems: HfF_4 - BaF_2 - ThF_4 and ZrF_4 - ThF_4 - BaF_2 . Preliminary measurements indicate that the scattering is larger for the HfF_4 glass than for the ThF_4 glass. Whether this is fundamentally due to the "fictive temperature" of these glasses or is extrinsic, remains to be seen after further measurements on a number of samples are performed. In addition, Raman scattering measurements were made on

these systems as a means of identifying the optical phonons in the glasses compared to the phonons of the pure constituents of the glasses.

4. Surface Polaritons [6,7]

Optical attenuated total internal reflection measurements were performed on the surface polariton of n^+ silicon and copper. These investigations enable the optical constants of the materials to be determined in a spectral regime where they are difficult to measure by conventional means and, in addition, the dispersion relationship of the surface excitations were obtained. The general dispersion relationship for surface plasmon at an air-solid interface is $k_{11}^2 = (\omega^2/c^2)(\epsilon(\omega))/(1+\epsilon(\omega))$ where $\epsilon(\omega)$ is the complex bulk dielectric function of the solid. In general, there will be two physical solutions to the dispersion relationship, that is, one where the frequency is real and k_{11} complex; and the other where ω is complex and k_{11} real. Up to the present work, there were wide discrepancies between theoretical and observed dispersion curves obtained by attenuated total internal reflection techniques. Previously, investigators had attempted to interpret their data using real values of ω . Due to the apparent discrepancies between theoretical predictions and experimental evaluations in the real frequency phase, we examined the surface polariton dispersion relationship for various models in the complex frequency plane. An original method was developed to evaluate the optical constants, dielectric functions, and the Fresnel reflection coefficients by redefining them as functions of complex frequency. By evaluating the attenuated total internal reflection dispersion curves in the complex plane, we were able to obtain agreement between theory and experiment for the materials measured in this work. Before this analysis, it was believed that the backbending observed in some dispersion curves would occur only for complex wavevector solutions of the dispersion

relationship. Our analysis comparing the complex- ω and complex- k solutions of the dispersion relationship showed that the difference between the two calculations is small.

As a consequence of this work, we believe that all studies of surface polaritons should be conducted in the complex frequency plane when either the damping is large or there exists interband transitions in the spectral region studied.

5. Deep Level Derivative Spectroscopy [8,14].

Since our infrared wavelength modulation has proved so successful in studying volume and surface impurities in the alkali halides and alkali earth fluorides, of interest to high power laser components, we turned our attention to the use of this technique for the study of deep levels in GaAs and InP, of interest for high-frequency low-noise FET's.

Our infrared wavelength modulation spectrometer system is capable of measuring changes in the absorption or reflection of 1 part in 10^5 in the spectral region from 0.2 - 20 μm . The system consists of a modified grating monochromator. The modulation of the wavelength is accomplished by oscillating an output diagonal mirror similar to the system employed in the visible; this method of modulation is equally good for any wavelength in the spectral range of the monochromator and the amplitude of wavelength modulation can be continuously varied by up to $\Delta\lambda/\lambda \sim 10^{-2}$. The wavelength modulation technique yields essentially the energy derivative of the absorption coefficient. To obtain the absolute value of the absorption coefficient, one numerically integrates the observed derivative spectra and the constant of integration is supplied by a direct loss measurement in the same apparatus at a fixed wavelength where the absorption can be measured with good precision. The

system implementing the above operation is under microprocessor control. The detector presently employed for the infrared is a liquid nitrogen-cooled PbSnTe with a globar source for the spectral region from 2 to 12 microns. This system can be used equally well in the ultraviolet, visible, and infrared regions with appropriate changes of sources, gratings, and detectors.

We have demonstrated that infrared wavelength modulation absorption can detect deep impurity concentrations at levels of 10^{12} - $10^{14}/\text{cm}^3$ in semiconductors; previously, it had only been possible to study such concentrations by junction DLTS techniques and consequently it was not possible to observe absorption thresholds and excited states of deep impurities. An extensive study has been made on semi-insulating GaAs substrates in the spectral region from 0.5 - 1.4 eV prepared by various growth techniques. We have observed extensive fine structures with variations in absorption coefficients -- $\Delta K \sim 10^{-1} - 10^{-2} \text{ cm}^{-1}$ -- out of a relatively smooth background absorption of $1\text{-}2 \text{ cm}^{-1}$. Previously conventional optical absorption measurements reported in the literature have revealed a few plateau structures, indicating that they have only observed the envelope of absorption in this region. The relative magnitudes and the detail structure at 300°K varies from sample to sample, although the dominant structures are similar. The results are discussed in terms of excited states of various deep levels.

A detailed study of the derivative absorption spectroscopy of GaAs:Cr has been completed. The detailed extensive fine structure observed for the first time out of previously observed smooth absorption observed by conventional absorption techniques was correlated with a proposed energy level scheme of (Cr^{3+} - Cr^{2+}) ions in GaAs. This work has indicated that a comparable number of Cr ions are at tetragonal and trigonal sites.

This work is being continued on GaAs and InP prepared by various material

preparation techniques.

6. Determination of Homogeneity of Doping, Alloy Composition, and Strain.

In the growth of semiconductor layers by various epitaxial techniques such as M.B.E., L.P.E., and C.V.D., and the doping of layers by ion implantation and other techniques, an important technological problem is the assessment of the homogeneity of doping, alloy composition, and strain in the layers. We have used our wavelength techniques to determine shifts in various critical points as a function of doping and strain in several semiconductors.

One of the major fabrication processes used in the fabrication of n-type channel FET's on semiconducting GaAs is the utilization of ion implantation. The assessment of defects subsequent to implantation and annealing is of prime importance, especially so for shallow implanted layers $\sim 1000 \text{ \AA}$. We have observed the effects of ion implantation by the nondestructive methods of wavelength modulation and Raman scattering. Local strain was observed by measuring the shift of the imaginary part of the dielectric function of GaAs in the neighborhood of the E_1 and $E_1 + \Delta$ critical point. Implants of Be, Sb, S, In, and double implanted Sb and Be were studied; the implanting fluxes were of the order of $10^{13}/\text{cm}^2$, compared to ion unimplanted GaAs, positive and negative shifts of the energy of the critical point were observed, indicating that we are able to distinguish contraction or expansion of the lattice.

In addition, we found that the intensity of ϵ_2 the imaginary part of the dielectric function at the $E_1 + \Delta$ critical point decreased as a function of n-type doping. These results can be interpreted in terms of screening of the hyperbolic exciton associated with this critical point.

7. Oxygen in Silicon [15].

Oxygen impurities play a ubiquitous role in Si device fabrication which is still not fully understood. The limit of detectability of oxygen by conventional techniques is 0.1 ppm or $5 \times 10^{15}/\text{cm}^3$. It is conjectured that oxygen below this level can influence device performance depending upon the heat treatment. Heat treatment in the range $T = 450^\circ\text{C}$ results in kinetic changes in the concentration of "thermal" donors. We have shown that we have the sensitivity by our wavelength modulation technique to detect oxygen at levels of the order of $3 \times 10^{12}/\text{cm}^3$, i.e., if anyone has produced such oxygen-free samples!

It has been proposed for the formation of SiO_4 complexes in Si which explains the formation of "thermal" donors for heat treatment at $T = 450^\circ\text{C}$. The evidence that SiO_4 complex particles are formed is shown by the doublet nature of the spectra near $9 \mu\text{m}$ at room temperature rather than the single line which is usually seen for "free" SiO_2 . These transformations are seen at oxygen concentrations of the order of $1 \times 10^{18}/\text{cm}^3$ and it has been conjectured that only at these high concentrations is the "bound" state of SiO_2 formed. We have shown that SiO_4 precipitates can also be formed at much lower concentrations.

The usual method of detecting the oxygen content of floating zone crystals is to employ a differential infrared absorption method on a conventional double beam spectrometer and measure the absorption band at 1130 cm^{-1} ($9 \mu\text{m}$) relative to a known oxygen containing samples whose oxygen content has been previously analyzed by mass spectrometry. The detection limit by this method is 0.1 ppm representing $5 \times 10^{15}/\text{cm}^3$ which yields an optical absorption coefficient of $2 \times 10^{-2} \text{ cm}^{-1}$. Floating zone crystals which have received a minimum of three

zone vacuum passes generally reveal no oxygen concentration above the detection limit. However, some of these crystals, when subject to thermal processing, show device deterioration. Since conventional methods could detect no oxygen, the culprit could not be specified.

Since our wavelength modulation system can detect changes in absorption coefficient of the order 10^{-5} cm^{-1} for a 1 cm path length, we are in a position to extend the detection limit for oxygen to $2.5 \times 10^{12} / \text{cm}^3$. In all floating zone crystals examined which were obtained from the Hughes Industrial Products Division at Carlsbad, we were able to detect oxygen at levels of $10^{14} / \text{cm}^3$ by measuring the derivative of the $9 \mu\text{m}$ band relative to the derivative of a known standard.

The observed structure of the band is a multiplet rather than a single peak, indicating that the oxygen was precipitated as finely dispersed SiO_4 second-phase particles and not as SiO_2 "quasi-molecules" as had been previously conjectured for these low oxygen concentrations; such complexes were only previously observed at high oxygen concentrations, i.e., $\sim 10^{18} / \text{cm}^3$. These results indicate that oxygen precipitates in a heterogeneous nucleation process resulting in the formation of SiO_4 complexes.

The importance of our observation that oxygen may be bound to second-phase particles even at low oxygen concentrations for certain heat treatments has wide ramifications for silicon device fabrication. By various heat treatments, phase changes can alter the relative positions of the SiO_4 structure which may result in isolated free charged SiO_4 complexes which can be responsible for increase in "thermal" donors.

8. Surface Oxides [15].

Extensive studies exist by conventional infrared absorption techniques of the growth of oxide film on silicon which have a sensitivity limit of $\sim 2000 \text{ \AA}$. However, in order to understand the growth of native oxides, it is necessary to study films in the monolayer regime. There is evidence that at the Si-SiO_2 interface there is a native oxide of the order of 6 \AA whose structure is different from thick films.

We have shown by using our infrared wavelength modulation system that we can detect the 9.0 \mu m SiO band in 10 \AA layers with a signal-to-noise ratio of 100 to 1. Thus we have the capabilities of studying a fraction of a monolayer. There is a great current interest in surface passivation methods for GaAs. To this end we have used our wavelength modulation techniques to examine various oxide layers in GaAs and have found that we can easily detect OH and H_2O in these films.

This work is being continued for the study of oxides on GaAs and InP prepared by various techniques.

9. Fully Electric Servo Circuitry for Wavelength Modulation Spectroscopy [10].

In our visible wavelength modulated spectrometer, we have formerly employed quasi-mechanical systems to normalize the background variations due to light sources and detector spectral response. We have developed electronic circuits which replace the mechanical servos and lock-in amplifiers. The result is a faster response and wider range of gain while maintaining a constant photomultiplier tube voltage.

10. De-Correlation Technique for Separation of Drude Parameters from Wavelength Modulation Data [9].

Separation of bound and free electron contributions to the dielectric function is necessary for an accurate analysis of interband transitions, a technique for doing this separation which does not require low energy data was developed. The technique makes use of the fact that the functions which describe the contributions of each part are sufficiently uncorrelated, allowing the construction of a correlation function which uses the Drude effective mass and Drude relaxation time as adjustable parameters. The technique is shown to properly separate a test function and to yield reasonable results from experimental data.

11. Photoinduced Transients Spectroscopy.

The high electron mobility of GaAs and InP compared to Si results in higher device transconductance and, consequently, higher speed devices. Semi-insulating GaAs and InP substrates are desirable to reduce parasitics. Deep traps in the active layer may be introduced during technological processing.

Although DLTS techniques have been extensively employed to study deep levels in low resistivity material where junctions can be formed, the very large depletion layers on semi-insulating materials mitigates the use of junction techniques. However, such high resistivity material can be studied by the techniques of photoinduced transients spectroscopy (P.I.T.S.) employing our computer controlled system.

Photoinduced transients spectroscopy (P.I.T.S.) techniques involve the detection of current decay due to the emission of trapped carriers after illumination by chopped band gap light. In brief, excess electron-hole pairs

are optically generated in high-resistivity semiconductors by an intrinsic light pulse. After the light pulse, a transient current due to de-trapping of carriers from deep levels can be observed between two ohmic electrodes. The current decay is usually sampled at two fixed time intervals as a function of temperature; the procedure is repeated for a range of sampling times. By plotting the difference logarithmically as a function of temperature, peaks occur when the trap emission rate is equal to the sampling rate in the case of discrete levels. Hence by varying the sampling time and observing the peaks at a given temperature, the trap energy and thermal emission cross sections of the deep levels can be determined. Such a procedure which has been employed by previous investigators is extremely time consuming.

In our system, the apparatus is controlled by a LSI/11/23 computer which controls the light pulse, controls and varies the temperature, and digitizes the complete current transient and computes, on-line, the parameters of the deep levels. This system is a great time saver since for a single temperature sweep 100 time intervals are measured and signal averaged. Since the complete transient is measured, rather than the usual double gate measurement which assumes an exponential decay, we can distinguish non-exponential decays due to multiple levels.

With our P.I.T.S. system, previously described, we have studied semi-insulating GaAs produced by various growth techniques. In parallel, infrared wavelength modulation absorption on the same sample as the P.I.T.S. measurement was performed. The use of both techniques enables a correlation of the level positions by optical absorption cross sections as well as thermal emission rates from levels and consequently enable a better contact with theories of deep levels.

P.I.T.S. experiments were performed on a variety of semi-insulating

samples prepared by various epitaxial growth techniques such as M.B.E., C.V.D., L.P.E., as well as bulk samples grown by liquid encapsulation Czochozski (L.E.C.). Levels characteristic of the different material syntheses have been identified. Some of the levels are due to different impurities incorporated from run to run, while some of the levels appear to be intrinsic defects and defect impurity complexes due to non-stoichiometry. The above results are being correlated with various growth parameters coupled with analyses of S.I.M.S. and Hall measurements on the samples. This phase of the work indicates the close liaison necessary between measurements, syntheses, and sample preparation groups.

12. Light Scattering from Semiconductors.

The oxides that are formed on compound semiconductors in normal laboratory ambients or by deliberate preparation by various techniques are of fundamental as well as technological interest. The successful fabrication of MOS-type of devices as well as the stabilization of surfaces with few surface states depends upon the preparation of appropriate oxides. We have initiated Raman scattering studies from oxides on substrates of GaAs and InP both thermally grown or anodically prepared. Concomitantly with the Raman backscattering studies, we have used our wavelength modulation techniques to study the nature of the oxides of GaAs and InP. We have previously shown, using our infrared wavelength modulation system that it is possible to detect a $9.0\text{ }\mu\text{m}$ SiO band in an $8\text{ }\text{\AA}$ layer with a signal-to-noise of 100/1; consequently, we have the capabilities of studying a fraction of a monolayer.

The Raman scattering from ion implanted GaAs was studied in parallel with the wavelength modulation reflectivity experiments in the neighborhood of the $E_1 + \Delta$ critical point previously described. Changes in the first-order

longitudinal (LO) and transverse (TO) modes as well as two-phonon bands were observed in ion implanted material with Be, Sb, S, and In which could be correlated with the strain effects observed using wavelength modulated reflectivity.

The Raman spectra of anodically prepared oxides on GaAs reveal the presence of crystalline and amorphous arsenic at the interface whose concentration depends upon the heat treatment. These metalloids have a good Raman cross section which seems to be enhanced by their optical absorption. However, the scattering cross sections for the constituents of the oxide are small due to the transparency of the films and thick films have to be prepared for the scattering experiments. In such cases we have used our infrared modulation absorption system which has a sensitivity of a fraction of a monolayer. In examining the oxides grown on GaAs, it has been possible to detect OH^- modes in $0.5 \mu\text{m}$ layers.

13. Optical Properties of Order-Disorder in Metals [11,12,13].

Although the dominant thrust of this program involved the study of insulators and semiconductors, some work was completed on order-disorder effects on the band structure of metals. This work shows the power of optical derivative techniques for the study of metals. With the beginning of use of NiSi and PdSi in the microelectronic industry, the technique should prove useful for the study of thin Schottky barriers made from these and similar metals.

Wavelength-modulated derivative spectra of the reflectivity of $\beta' - \text{Cu}_x\text{Zn}_{1-x}$ has been determined between 1.5 and 5.1 eV for compositions near the $\beta' \leftrightarrow \alpha + \beta'$ phase transition. The alloys have been annealed and quenched in the β' phase on both sides of the phase transition. Both the intraband and interband properties

show marked changes at the transition. The Drude effective mass increases dramatically for the β' phase in the region where $\alpha + \beta'$ composition is thermodynamically preferred, indicating flattening of the bands. Shifts in interband properties at the transition confirm this interpretation and indicate that there are competing physical mechanisms which cause these shifts.

Derivative spectra of the optical properties of β' -AuZn have been obtained using wavelength-modulated spectroscopy between 1.5 and 5.1 eV. Assignments were made for interband transition at the M point of the Brillouin zone which fix the transition energies with an accuracy previously unattained. Some relative values of oscillator strengths have also been determined.

The optical properties of α phase $\text{Ag}_{0.7}\text{Zn}_{0.3}$ have been determined near the optical absorption edge. This alloy composition eliminates the sharp Ag plasma resonance. The band shifts which are observed are in qualitative agreement with calculations which have been performed for the similar alloy, $\alpha\text{-Cu}_{0.7}\text{Zn}_{0.3}$.

C. PUBLICATIONS FOR THIS PERIOD

1. "Wavelength Modulation Spectroscopy of Highly Transparent Solids," R. Braunstein, R. K. Kim, and M. Braunstein, NBS Special Publication 568, U.S. Government Printing Office, Washington, D.C. 1979.
2. "Infrared Transparent Glasses Derived from the Fluorides of Zirconium, Thorium, and Barium," Mat. Res. Bull. 15, 735 (1980).
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12. "Wavelength Modulated Spectra of α - $\text{Ag}_{0.7}\text{Zn}_{0.3}$ Near the Optical Absorption Edge," R. Stearns, R. Braunstein, and L. Muldower [in preparation for Phys. Status Solidi].
13. "Optical Properties of β' -AuZn by Wavelength Modulated Derivative Spectroscopy," R. Stearns, R. Braunstein, and L. Muldower [in preparation for Phys. Status Solidi].

14. "Wavelength Modulation Spectroscopy of Highly Transparent Solids," R. K. Kim and R. Braunstein [in preparation for J. Applied Optics].
15. "Oxygen in Floating Zone Silicon," R. K. Kim and R. Braunstein [in preparation for J. Applied Physics].

D. PARTICIPATING SCIENTIFIC PERSONNEL

Bradley Bobbs	Ph.D. Candidate
Michael Burd	Ph.D. Candidate
Donald Deal	Ph.D. granted June 1982. Thesis: "Raman and Brillouin Scattering in Glasses"
M. Eetemadi	Ph.D. Candidate
R. K. Kim	Ph.D. to be granted June 1983. Thesis: "Infrared Wavelength Modulation Spectroscopy of Highly Transparent Solids"
Robert Martin	Ph.D. Candidate
Ronald Stearns	Ph.D. granted June 1982. Thesis: "Order-Disorder in Metals"

E. SCIENTIFIC INTERACTIONS

Liaisons were maintained with synthesis groups involved in laser window problems. Collaborative endeavors were pursued with the M. Braunstein group at the Hughes Research Laboratory who are involved in the synthesis of alkali halides by reactive atmosphere processing techniques. These interactions have involved a continual exchange of samples and a feedback of measurement results from the wavelength modulation and Rayleigh-Brillouin scattering experiments. Discussions were held with M. Bass and S. Allen of the Center for Laser Studies at USC regarding the use of our wavelength modulation apparatus to investigate the optical properties of their materials strengthened by formation of point defect complexes and surface compressive layers. Arrangements were made for joint visits. Discussions were held with Major Harry Windsor of DARPA and the Bennett group at China Lake regarding the use of our techniques for studying OH in film coatings and the development of our technique for studying low level absorption in optical fibers. Discussions were held with A. Vaidyanathan and A. H. Guenther of the Air Force Weapons Laboratory, Kirtland AFB, regarding calculations of the two-photon absorption in direct band gap materials. It is now found that our original perturbation calculation is consistent with Keldysch's strong field calculations and the discrepancy between the Braunstein and Basov results have been resolved by noting several errors in the Basov results.

We have continued active relationships with groups in the semiconductor area. These have included: C. Krumm and D. Matthews and the Hughes Research Laboratory regarding deep levels in high frequency FET's of GaAs; C. Liton and K. Bajaj of Wright Patterson Air Force Base concerning modulated structures; D. Bode and C. Jones on problems of deep levels and FET's; Prof. Modukhar of

USC on deep level problems.

Invited Papers and Seminars

Invited Paper	Laser Damage in Optical Materials, "Wavelength Modulation Spectroscopy," NBS Boulder, Co., Oct. 1979.
Seminar	Physics Dept., U.C. Irvine, "Optical Properties of Glasses," Oct. 1980.
Invited Paper	Laser Damage Symposium, NBS Boulder, Co., Oct. 1980. "Wavelength Modulation of Laser Window Materials"
Seminar	Physics Dept., Long Beach State College, "Optical Properties of Glass," Nov. 1980.
Seminar	Laser Institute, University of Southern California, "Wavelength Modulation Spectroscopy," March 1981.
Invited Paper	16th International Conference on the Physics of Semiconductors, Aug. 1982, "Derivative Spectroscopy of GaAs:Cr"
Seminar	Physics Dept., Long Beach State College, Feb. 1983. "Derivative Spectroscopy of Semiconductors"

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