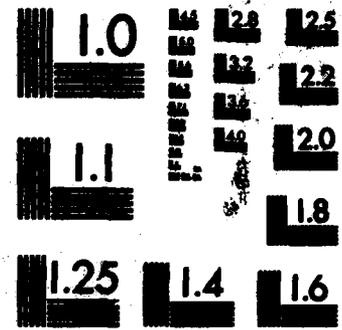
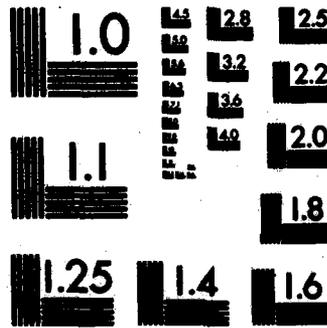


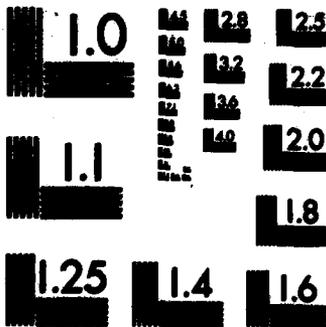
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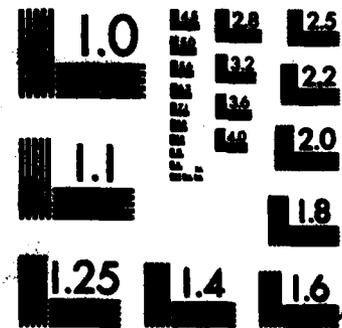
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ADA 120788

AFWAL-TR-81-4151

NEW X-LEVEL DETECTORS

HONEYWELL CORPORATE TECHNOLOGY CENTER
10701 LYNDALE AVENUE SOUTH
BLOOMINGTON, MN 55420

JANUARY 1982

FINAL REPORT FOR PERIOD 1 JUNE 1980 THROUGH 31 MAY 1981

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MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
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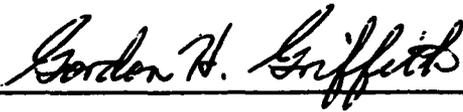
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This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The objectives of this program were to determine the feasibility of using the In-X center in silicon as the active level in a photoconductive device for the 8-14 micron atmospheric window and to clarify the role, if any, which aluminum plays in the formation of the In-X defect. Most evidence points to the In-X center being an indium-carbon complex which shows a mass-action type behavior but there is some speculation that In and Al constitute the defect and that carbon stabilizes this association.		

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To utilize the In-X level in an efficient photoconductive device requires concentration of the In-X defect in the $5-10 \times 10^{16} \text{ cm}^{-3}$ range. To achieve these concentrations, near maximum concentrations of indium and carbon in silicon are required. The gradient transport solution growth method of crystal growth was adopted to dope the silicon with near maximum amounts of In and C.

Material from Si(In,C) growth runs were then subjected to a variety of low temperature heat treatments ($<600\text{C}$) to study the reaction kinetics of the In-X center. This was done to determine if suitable concentrations of In-X could be obtained in reasonable annealing times. It was found that, contrary to the mass action law, the concentrations of In-X centers decreased with increased annealing times. Concurrent with this decrease in In-X concentration was a dramatic decrease in carbon concentration. Evidence from infrared absorption measurements shows that the carbon may be complexing with oxygen and also precipitating in the form of SiC microprecipitates. Because of the role of C in the In-X center, this reduction in C concentration inhibits the formation of In-X centers.

Si(In,Al) crystals were grown by the Czochralski technique to study the effects of Al on In-x formation. Infrared absorption measurements were performed on a number of Si(In,Al) crystals which were annealed at a variety of temperatures. The In-X concentration was monitored and compared to that expected from the law of mass action. We find that the presence of Al does not enhance In-X formation but actually suppresses it when compared to Si(In) Czochralski crystals.

We conclude that the In-X center in silicon does not offer a viable choice as an active level in a photoconductive device.

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FOREWORD

This final report describes work performed by personnel of the Honeywell Corporate Technology Center, 10701 Lyndale Avenue South, Bloomington, Minnesota 55420 during the period 1 June 1980 through May 31, 1981 under Contract F33615-80-C-5026. The program was monitored by G.H. Griffith, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio.

The program was directed toward showing the feasibility of using the In-X level in Si as the active level in a photoconductive device for the 8-14 m atmospheric window. The following people have contributed significantly to the work reported here: S. Dietz, R. Hager, T. Madsen, T. Novak, D. Schafer, and J. Sjerven.

An administrative form with several sections. The top section contains a date stamp "MAY 1981" and a signature. Below this are several empty rectangular boxes. At the bottom of the form, there is a large, handwritten letter "A".

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I. INTRODUCTION

A. Search for photodetective devices

The emphasis on development of photoactive devices in the infrared region of the electromagnetic spectrum has centered in the past on intrinsic semiconducting materials such as HgCdTe and extrinsic silicon, that is, silicon doped with an impurity whose ionization energy corresponds to the photoactive region of interest. While intrinsic detectors like HgCdTe have many inherent advantages over doped silicon (such as higher operating temperature and better sensitivity), the vast technology which has been developed for large area silicon processing means that, if good quality silicon material were available, extrinsic silicon photodetectors should be easier and cheaper to make.

An ideal dopant in silicon from an infrared systems point of view would be one with an ionization energy at about 0.1 eV, so that the detector response would be matched to the 8-14 micron atmospheric transmission window. The standard extrinsic detector material for this region has been Si(Ga) ($E_i = 0.072\text{eV}$). However Si(Ga) suffers from having a long cutoff wavelength ($\lambda_{CO} = 17$ microns) thus requiring very low operating temperatures ($< 20\text{K}$). In some applications the extra cooling required to achieve 20K (as compared to 40K) results in a severe handicap for systems design. It would be desirable to have a detector material whose cutoff wavelength is more closely matched to the 8-14 micron region so that higher operating temperatures could be realized.

Several years ago, work on indium doped silicon for 3-8 micron photoconductive detectors led to the discovery of a new acceptor level in silicon related to the presence of indium and carbon and having an ionization energy of 0.1128 eV, considerably shallower than substitutional indium (0.156 eV) and an almost ideal match to the 8-14 micron window. This defect level, termed In-X, has been revealed in low temperature Hall data¹, in the photoconductive spectrum of Si(In)², and in optical absorption measurements.³ Subsequent measurements on other IIIA acceptors in silicon revealed similar levels.^{3,4}

The presence of In-X in Si(In) photoconductors introduced additional thermal noise into the detector thus necessitating a lower temperature of operation than is needed if these defects are absent. Consequently early investigations of the In-X level were carried out with the expressed intent of eliminating it from the doped silicon material so as to reduce the thermal noise. Because of its ionization energy, however, the possibility of using the In-X defect as the active level in a photoconductive device (for the 8-14 micron range) cannot be overlooked. As an alternative to Si(Ga) photodetectors a Si(In-X) device would offer the advantage of somewhat higher operating temperatures (~ 20K for Si(Ga) and ~ 40K for Si(In-X)).

A basic requirement for an efficient photoconductor is that the concentration of photoactive centers in the material be large enough to ensure a high probability of detection of an infrared photon. The actual concentration necessary depends on the dopant's photoionization cross section and the thickness of the active device. In the case of the In-X center we have the added factor that it is a complex related to the presence of both indium and

carbon. Thus to determine the conditions in which an adequate content of In-X centers in silicon can be achieved for efficient device performance requires a knowledge of the center's basic properties.

B. The In-X center in silicon⁵

The X-center in indium doped silicon has been found to exist in concentrations of 10^{-2} to 10^{-4} times that of the indium concentration in pulled crystals. In-X shows no dependence on oxygen, boron, or more than one indium atom per complex. Equilibrium data does indicate that the X-center depends on a single carbon atom per complex. Empirically the relationship between In-X, In, and C has been found to follow a mass-action relationship for pulled crystals

$$K(T) = \frac{[\text{In-X}]}{[\text{In}] \cdot [\text{C}]} = K_0 \exp(\Delta H/KT) \quad (1)$$

where the brackets denote concentrations, H is the heat of formation, and T is the annealing temperature. K(T) is the chemical equilibrium constant describing the reaction



The In-X concentration can be raised or lowered in a continuous and reversible manner by annealing the material at various temperatures. Equilibrium annealing data for the In-X center is presented in Figure 1 and Table 1 along with similar annealing data for the boron, aluminum and gallium X-centers.

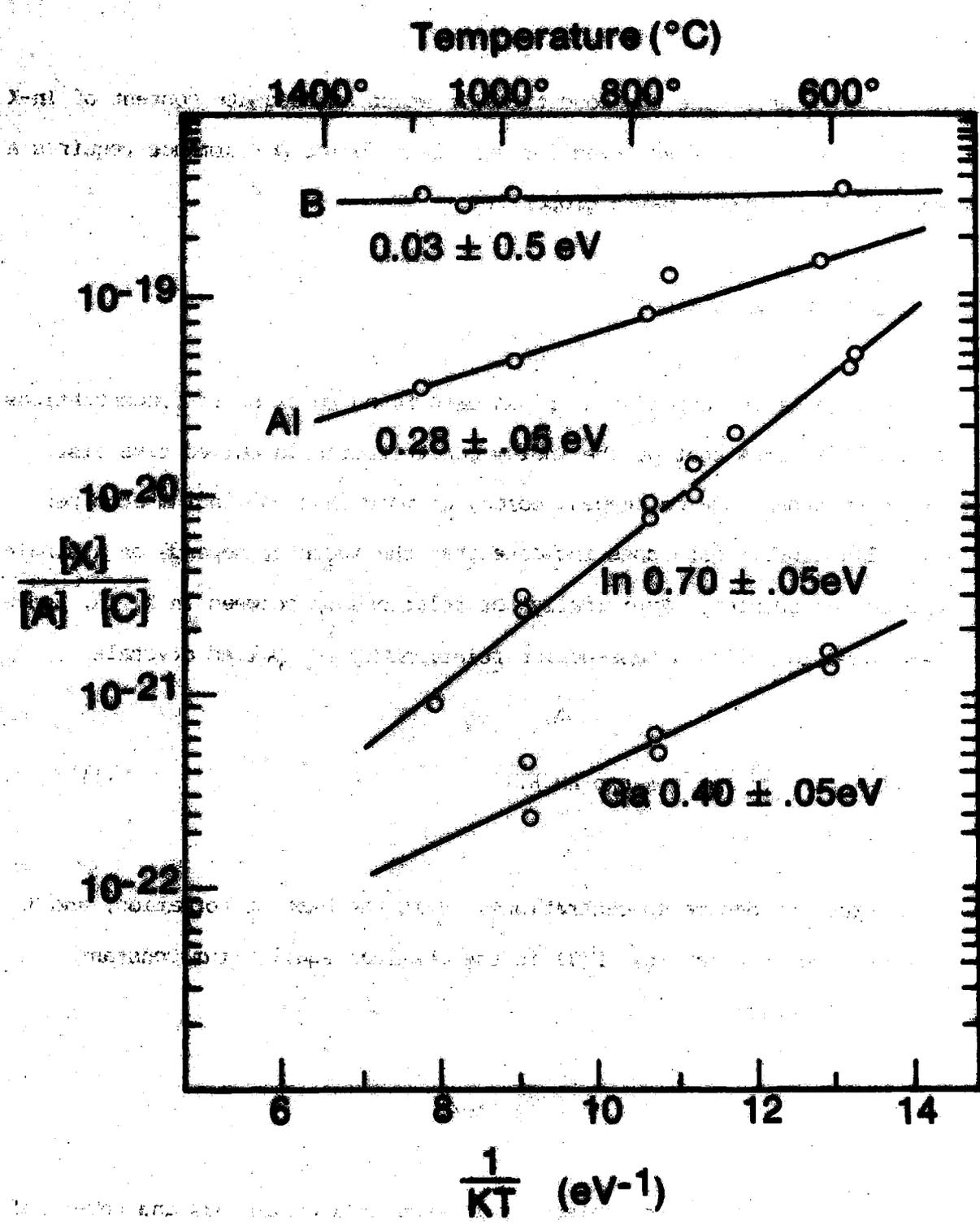


Figure 1. Dependence of X center concentration on annealing temperature, plotted to test a mass-action relationship with the acceptor and carbon concentrations.

None of the X-centers anneals out up to the melting point of silicon. The overall increase in the heat of formation in passing from the lightest to heaviest IIIA element is consistent with a strain relief explanation of impurity pairs. This explanation suggests that for a substitutional atom larger than silicon, like In, the surrounding lattice is strained outward around the impurity, whereas for a substitutional impurity smaller than silicon, like C, the surrounding lattice is pulled inward. The net strain effect in silicon containing both carbon and indium is expected to be minimized when the In and C atoms are grouped in pairs.

TABLE 1. X CENTER PARAMETERS

	H	Ko
B-X	.03 ± .05eV	2.6 x 10 ⁻¹⁹
Al-X	.28 ± .05eV	3.8 x 10 ⁻²¹
Ga-X	.40 ± .05eV	6.13 x 10 ⁻²⁴
In-X	.70 ± .05eV	3.63 x 10 ⁻²⁴

The idea of the X-center in silicon being a nearest neighbor substitutional carbon-acceptor pair is further enhanced by the recent uniaxial stress measurements of the Al-X center.⁶ The Al-X stress symmetry was determined to be that of a [111] trigonal defect. This rules out both single-atom defects and distant pairs. The high temperature stability and the cyclic annealability of the X-centers is not consistent with interstitial or vacancy-related defects. Furthermore, calculations⁵ using the extended Huckel

cluster technique give best agreement with experimental ionization energies when a nearest neighbor substitutional carbon-indium pair is assumed.

While most of the evidence points to the IIIA-X centers being substitutional IIIA-carbon complexes there is some speculation^{6a} that the centers may result from an interaction between unlike substitutional group IIIA impurities. For the In-X center it was supposed that indium and aluminum constituted the defect and that carbon played a role in the formation or stabilization of the association. It should be noted, however, that no appreciable amount of substitutional aluminum was seen⁵ in absorption spectra after high temperature anneals when the X-center is broken apart. We shall assume then that the substitutional In-C pair provides an adequate explanation of the In-X defect and base our arguments on detector requirements accordingly.

C. Photoconductive requirements for Si(In-X) detectors

The interest in In-X doped silicon as a photoconductive material arises because the ionization energy of the In-X level is suitably matched to the 8-14 micron spectral window. We shall now consider the basic requirements for an efficient Si(In-X) photoconductor.

To optimize detector performance it is necessary to maximize the quantum efficiency η , i.e., the number of excess carriers produced per absorbed photon.

The quantum efficiency is defined as

$$\eta = \frac{(1-r) (1-\exp(-\alpha d))}{1-r \cdot \exp(\alpha d)} \quad (2)$$

where α is the absorption coefficient at wavelength λ and r is the reflectivity of the material (silicon in our case). To simplify the discussion we assume no reflection of the incident radiation at the front surface of the photoconductor. This in effect puts an upper limit to the quantum efficiency of the device. Equation (2) then becomes

$$\eta = 1 - \exp(-f d) \quad (3)$$

where we have introduced the factor f to describe the reflectivity of the unabsorbed radiation at the back surface of the photoconductor. For the case where r is unity at the back surface $f = 2$ whereas when $r = 0$ then $f = 1$. The absorption coefficient α for the In-X level can be written as

$$\alpha = [\text{In-X}] \cdot \sigma_{\text{In-X}} \quad (4)$$

where $\sigma_{\text{In-X}}$ is the optical cross section of the In-X centers. $\sigma_{\text{In-X}}$ may be estimated from the empirical relation

$$\sigma_i = \frac{2.5 \times 10^{-18}}{E_i^2}$$

which describes the photoionization of IIIA acceptors in silicon.⁷ E_i is the

ionization energy of the photoactive center. Using $E_{\text{In-X}} = .1128$ eV and assuming a detector thickness of .5mm we can determine from Equations (1) and (2) the quantum efficiency of a Si(In-X) photoconductor as a function of In-X concentration. This is shown in Figure 2. To achieve quantum efficiencies greater than 50% requires concentrations of In-X of the order of $5-10 \times 10^{16} \text{cm}^{-3}$.

According to Equation (1) the In-X concentration may be varied systematically by varying the annealing temperature of the material. Using data from previous studies⁵ of indium doped silicon and assuming the maximum solubility⁸ of indium and carbon in silicon the maximum concentration of In-X centers versus annealing temperature may be evaluated from Equation (1):

$$[\text{In-X}]_{\text{MAX}} = 4 \times 10^{12} \exp(.7\text{eV}/KT_{\text{MAX}}) \quad (5)$$

The maximum annealing temperature required to achieve a given concentration of In-X is plotted along the upper horizontal axis of Figure 2.

It is apparent from Equation (5) and Figure 2 that to achieve In-X concentrations suitable for efficient photodetectors (say $\eta = .5$) silicon must be doped with In and C near their maximum solubility limits and then annealed at temperatures lower than about 550C for a long enough time to achieve equilibrium conditions. Of course if the concentration of In and/or C in the Si is less than the maximum solubility limits then the annealing temperatures must be lower still to yield $[\text{In-X}] = 5-10 \times 10^{16} \text{cm}^{-3}$.

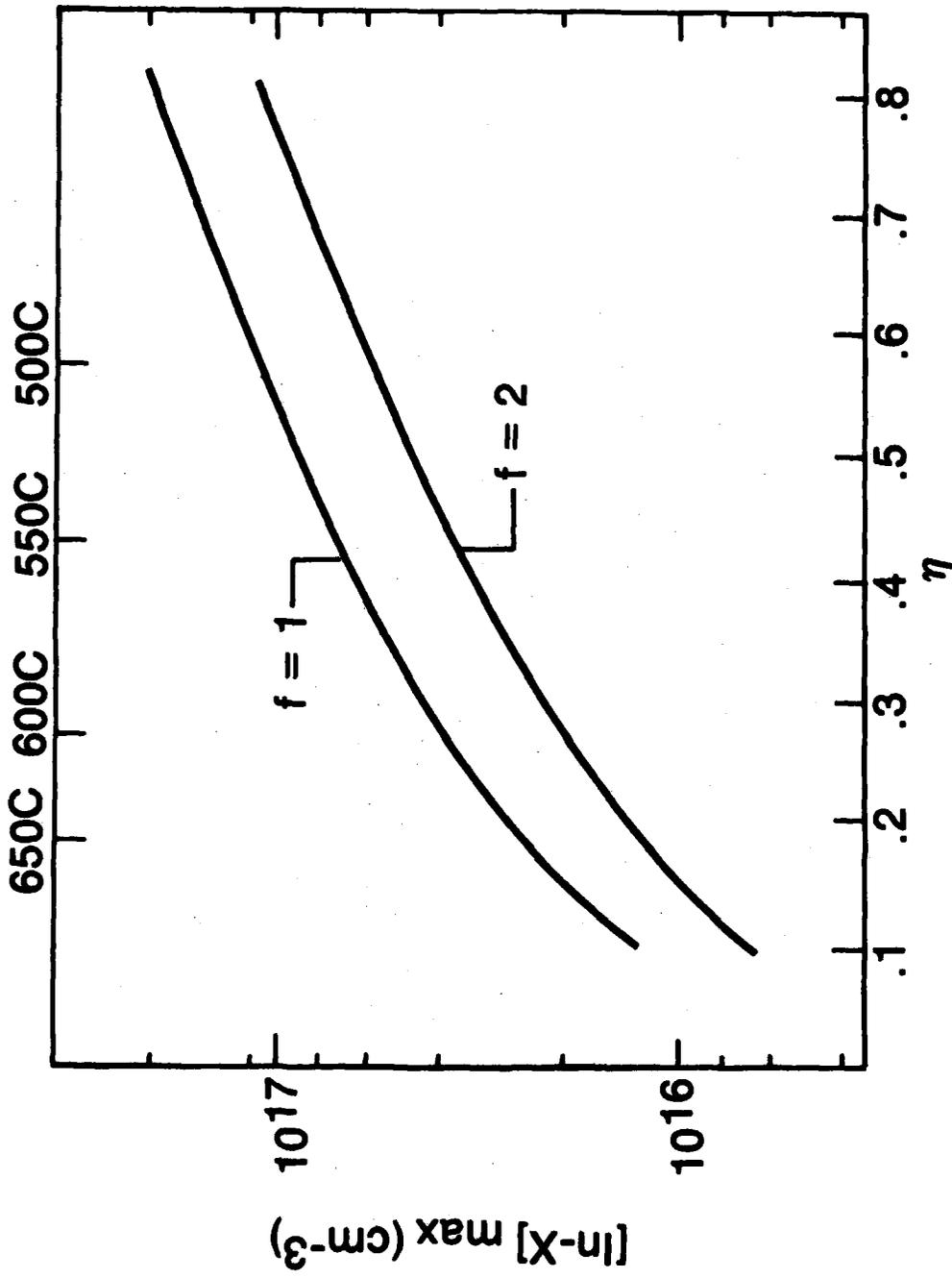


Figure 2. Quantum efficiency versus the concentration of In-X levels in a Si(In-X) photoconductor. $f=1$ implies total transmission of radiation at the back surface of the material while $f=2$ means total reflection. The upper horizontal scale shows the required annealing temperature to achieve a given N_{In-X} assuming maximum doping of In and C (using the $f=1$ case).

Previous studies¹⁻⁵ of the In-X centers in silicon dealt with concentrations of In and C less than In_{MAX} and C_{MAX} and with annealing temperatures greater than 600C. Typical annealing times to establish equilibrium of In-X were of the order of several hours. The concentrations of In-X centers obtained for the most part were in the $10^{14}cm^{-3}$ range. An investigation of the doping levels and annealing kinetics necessary to make Si(In-X) photoconductors had not been done.

The purpose of this program has been to investigate the feasibility of using the In-X center in silicon as the active level in a photoconductive device. Specifically the objectives have been:

- 1) to increase the In-X concentration to $5-10 \times 10^{16}cm^{-3}$
- 2) to determine the extent to which aluminum plays a role in the formation of the In-X complex.

Objective 1 entailed the growth of silicon doped with In and C near their maximum solubility limits and then performing low temperature annealing studies to increase the concentration of In-X. Concurrent with this was an attempt to understand the reaction kinetics of the In and C reaction. It is reasonable to expect the rate of formation of the In-X complex to decrease with decreasing temperature. As mentioned previously, equilibrium concentrations of In-X for $T_{anneal} > 600C$ were obtained after several hours of annealing. Using a rule of thumb of chemistry⁹ which estimates reaction rates double for every 10C increase in temperature, annealing times greater than 10^3

hours are indicated for equilibrium of In-X centers to occur at temperatures around 500C. Consequently, while In-X concentrations of $5-10 \times 10^{-16} \text{cm}^{-3}$ are possible in principle, the annealing times to achieve these concentrations may be so long as to become impractical. A knowledge of the kinetics of the In-X reaction would allow one to determine the feasibility of annealing at a temperature at which In-X concentration of the order of $5-10 \times 10^{-16} \text{cm}^{-3}$ could be achieved, but for which annealing times would not be prohibitively long.

Objective 2 was done to clarify our understanding of the In-X defect. While we believe the complex is that of an In-C pair, the somewhat tenuous evidence^{6a} for an Al-In complex stabilized by C cannot be discounted without further study. We have attempted therefore to study the Si(In,Al) system to measure the effects of Al on In-X.

II. EXPERIMENTAL PROCEDURES

A. Solution Growth of Si(In,C)

To achieve high doping concentrations of In-X requires doping silicon with near maximum solubility limits of both In and C. Any less In or C in the material will only require lower annealing temperatures and perhaps prohibitively long annealing times. The method by which we grow Si(In,C) crystals must then be appropriate to achieve these maximum doping limits.

Since indium exhibits retrograde solubility in silicon with the peak of the solubility curve occurring between 1300-1340C¹⁰, maximum doping of silicon

with indium requires growth temperatures of about 1320C. This precludes the use of Czochralski or float zone techniques since growth of crystals using these methods occurs near the melting points of Si (1410C) where the In solubility is much lower (see Figure 3). We have adopted the gradient transport solution¹¹ growth method to provide for maximum In concentrations in Si.

The principles¹¹ of solution growth are illustrated in Figure 4 using a binary phase diagram in which the two components of the system are silicon and indium. A silicon substrate is covered with the liquid metal (indium in our case) which in turn is covered with silicon source material. As indicated by the liquidus of the phase diagram, the metal has the capacity to dissolve appreciable amounts of silicon at high temperature; this solubility increases steadily with increasing temperature. A temperature gradient is now introduced in which the source is made slightly hotter than the substrate, and the solution tends to become richer in silicon near the source due to this increasing solubility of silicon in the solution with increasing temperature. The concentration gradient in the solution causes transport of silicon toward the substrate. At the substrate, the solution then tends to become supersaturated and thus deposits silicon there which is doped according to the dopant solubility at the substrate temperature. The process continues as long as the temperature gradient is maintained and source silicon is present. By fixing the substrate temperature near 1300C we can ensure that silicon will be deposited with the maximum In concentration possible. This temperature also guarantees near maximum solubility limits of carbon in the grown material when it is present in the solution.^{5,8}

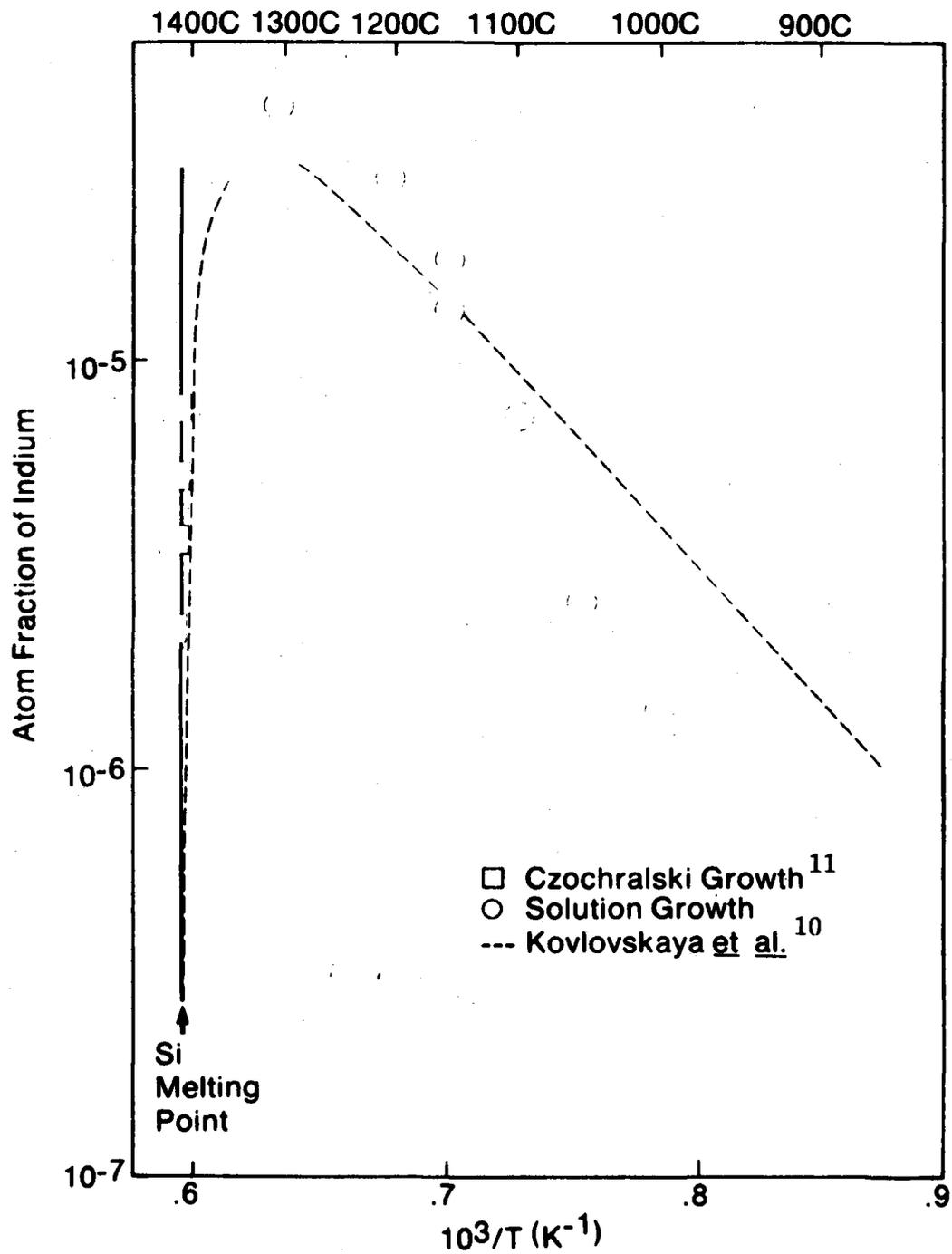


Figure 3. The solid solubility of indium in silicon versus temperature showing the retrograde behavior of indium.

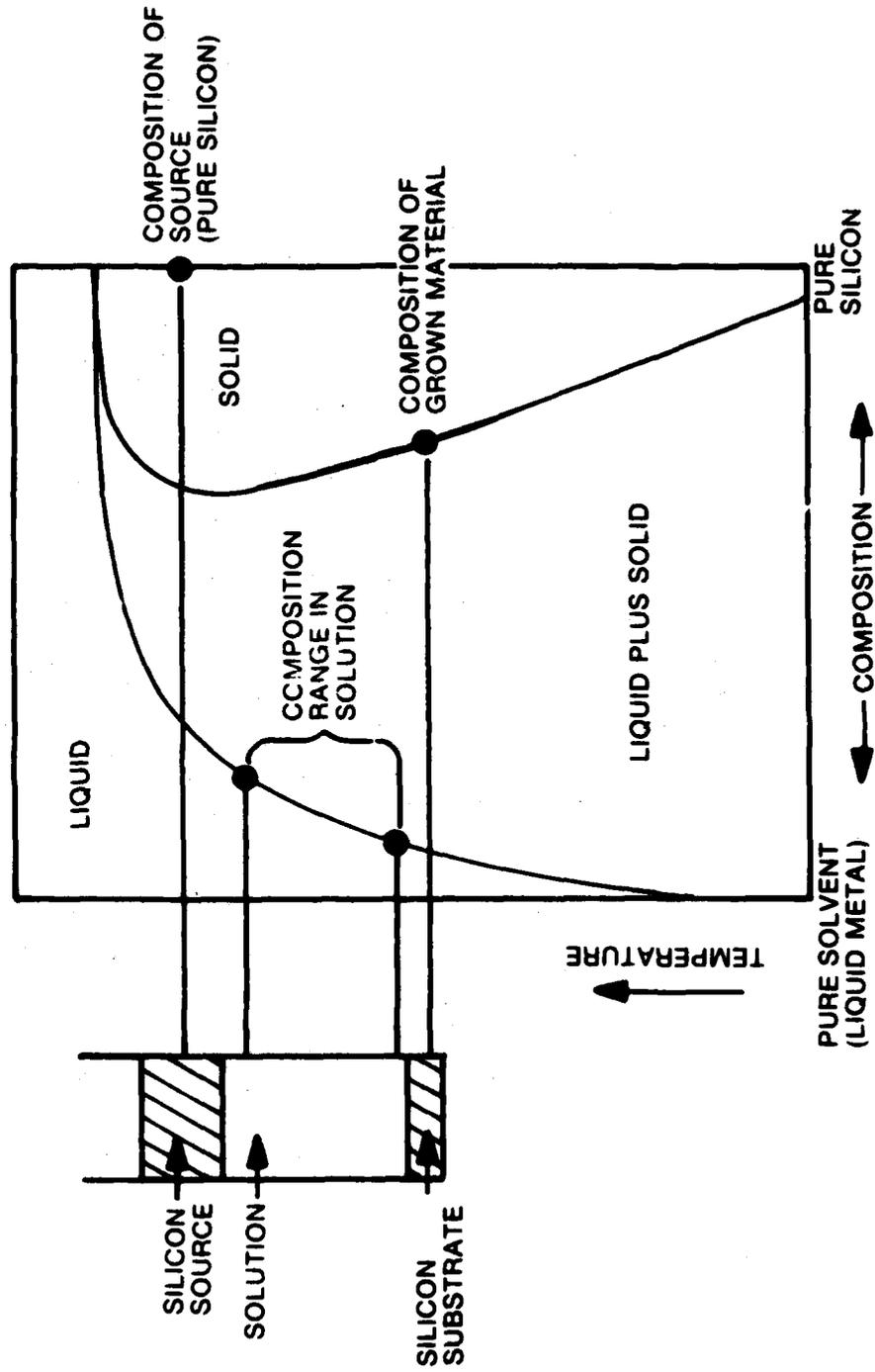


Figure 4. Principles of Gradient Transport Solution Growth

Besides the ability to achieve high doping concentrations of indium in silicon, the gradient transport approach initiating crystallization has several unique aspects which favor controlled growth and uniform doping of the grown material. First of all, the heat flow and mass transport patterns are stable, since there is no stirring or convection of the solution. Heat is carried primarily by conduction; in contrast to Czochralski growth, the absorption and release of the heat of fusion at the source and substrate is negligible, so that the temperature profile is largely independent of the fact that crystal growth occurs. The transport of silicon in the solution is carried out by diffusion. The density gradient associated with the silicon concentration gradient does not give rise to convection, since the silicon rich portion, which is less dense, is on top. A second aspect of the gradient transport approach is that it provides a means of inducing crystal growth with a minimum of supercooling. The series of composition and temperature values occurring at various positions in the solution during gradient transport tend to be fairly close to the silicon-solvent liquidus. By comparison, isothermal cooling of a saturated solution involves a greater degree of supersaturation for the same value of composition gradient or growth rate.

Since In does not wet to Si at temperatures less than about 1100C a preliminary wetting step was performed where the source In layer substrate was heated to ~1250C at which point the In would spread over the substrate surface and wet to the Si source and substrate. A silicon weight was placed on top of the source material to force the source and substrate together during this step. The wetting step was performed under dry N₂ or Ar gas in a sealed quartz vessel. The double well structure of the substrate was adopted so that

the inner solution layer would be isolated from outside impurities during the growth run.

After the wetting step the source/substrate assembly was X-rayed to ensure that the substrate had been covered uniformly with In. If the wetting step was deemed adequate, then the assembly was placed in a growth furnace setup shown in Figure 5.

The source and substrate material used for most of the growth runs was 100 Ω -cm p-type silicon of <111> orientation with typical concentrations given in Table 2. These impurities were determined by infrared absorption using the Digilab-14 FTS spectrometer. The C concentration found in these crystals were of sufficient value for the initial growth runs that no additional C was added. The purity of the In starting material was given by the manufacturer as six nines.

TABLE 2. TYPICAL IMPURITY CONCENTRATIONS IN 100 Ω -cm
p-TYPE SILICON USED FOR GROWTH MATERIAL

$$[C] = 1.4 \times 10^{17} \text{ cm}^{-3}$$

$$[B] = 4.2 \times 10^{13} \text{ cm}^{-3}$$

$$[O] = 2.3 \times 10^{17} \text{ cm}^{-3}$$

B. Czochralski Growth of Si(In,Al)

Although the maximum In doping levels reported in Czochralski silicon are

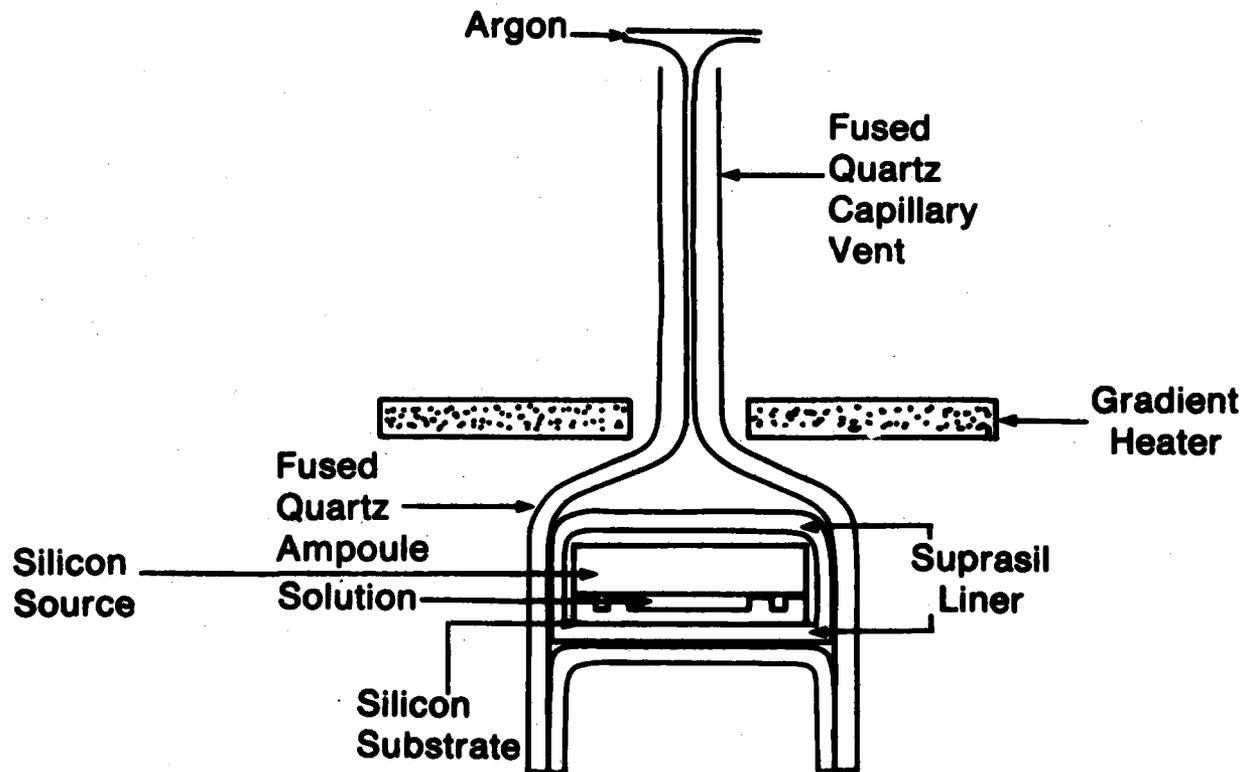


Figure 5. Experimental setup for the growth of Si(In,C) crystals by the gradient transport technique

about a factor of five below the solubility limit we have adopted this method of growth to investigate the role of Al in the formation of the In-X complex. Czochralski growth is a fast, well developed process and immediately capable of carrying out the double doping of Si with Al and In.

The Czochralski (CZ) growth technique¹² is outlined in Figure 6 which shows the growth setup. The first step is to melt a polycrystalline block of silicon in a crucible located inside a pulling chamber fabricated of refractory or water cooled materials which is either evacuated or filled with an inert gas, such as argon, of the desired pressure. Generally the crucible arrangement consists of a quartz inner crucible containing the melt and an outer crucible made of high purity graphite. The latter acts in this case as a susceptor for the quartz crucible. The charge is melted by resistance or rf heating. The required amount of dopant (In and Al in our case) is then added to the melt. A small portion of the seed crystal is then intentionally melted to ensure that the melt wets the seed. When thermal equilibrium is established the growth process is started with a slow withdrawal of the seed crystal from the melt in the vertical direction and simultaneous lowering of the melt temperature. This results in the material solidifying at the crystal-melt interface in the same crystalline form and orientation as that of the seed. The crystal diameter is subsequently increased by further lowering of the power input. Both the crystal and the crucible are generally rotated in order to minimize thermal asymmetry. The crystal thus acquires the shape of a cylinder. When the required diameter is reached the thermal conditions are adjusted such that this diameter is maintained. Typical silicon crystal diameters are 1 to 6 inches.

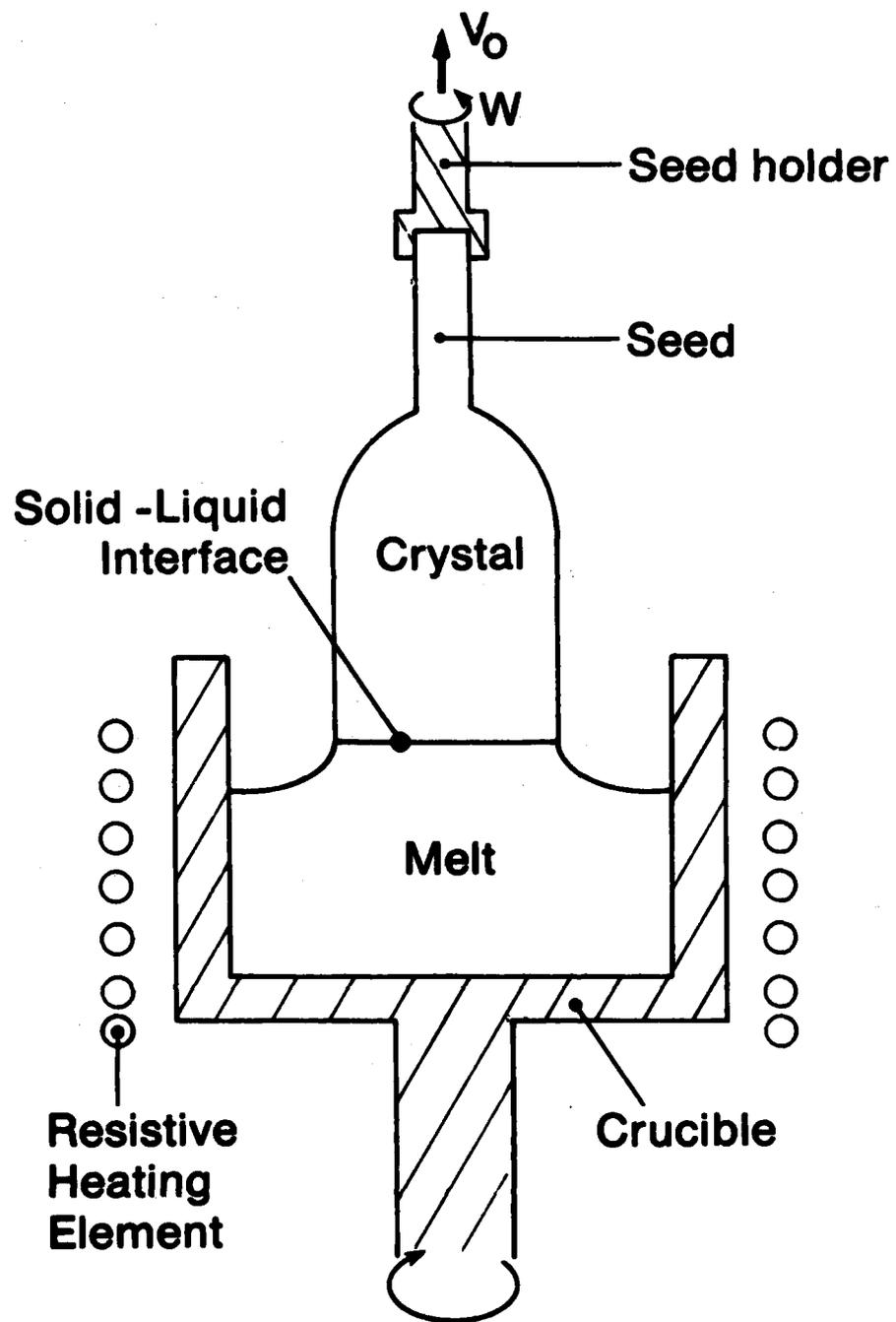


Figure 6. The Czochralski Growth Technique

For silicon the CZ technique has one great disadvantage. Because molten silicon is chemically very reactive, the direct contact between the melt and the wall of the quartz crucible causes contamination of the melt, particularly with oxygen. This results in relatively high concentrations of oxygen in the as grown crystals.

The crystal may also be contaminated by carbon originating from the graphite susceptor and heating element. Carbon concentrations in CZ Si between 10^{16} and $3 \times 10^{17} \text{ cm}^{-3}$ are common. Since we wish to have carbon in our grown samples this does not create a problem in the growth of Si(In,C) or Si(In,Al,C). As mentioned previously, to introduce C into our solution growth material we used CZ silicon for our source and substrate.

C. Preparation of Samples for Analysis

Following the growth of Si(In,C) or Si(In,Al,C) by solution growth or CZ techniques respectively, the grown material was wafered into slices typically 0.5-1 mm thick and then prepared for a variety of heat treatments and analyses. If the material was to be analyzed optically it was mechanically lapped and polished with about a $1/2^\circ$ taper to eliminate fringing effects. For Hall measurements the samples were mechanically lapped with fine alumina grit and then chemically polished. Then In electrical contacts were evaporated on the Hall samples and the samples were annealed at 750C to allow diffusion of the In into the Si. Following this preparation each Hall or optical sample was then annealed at a given temperature for a prescribed

amount of time under a dry N₂ atmosphere after which analysis by the Hall technique or IR absorption was undertaken.

D. Infrared Absorption by Fourier Transform Spectrometry

The infrared spectra of numerous shallow impurities in silicon have been known for many years and are explainable in terms of effective mass theory. The optical processes that may occur for both donor and acceptor centers include:

- o Transitions from the ground state of the impurity center to localized excited states, and
- o Transitions from the ground state of the impurity center to the continuum states of the nearest conduction or valence band.

The energy states due to impurities in silicon and some of the possible transitions are illustrated schematically in Figure 7. The donor impurities form localized levels with energies close to the conduction band, while the acceptors form levels near the top of both the V₁ and V₃ valence bands. For the donors, electrons can be optically excited from the ground state to the various excited states giving rise to a sharp line absorption spectrum. Similarly for acceptors, the holes can be excited to the various excited states resulting in a sharp line absorption spectrum such as shown in Figure 7 for a silicon sample with 3.5x10¹⁵ cm⁻³ of In-X. The absorption lines are due to transitions to the P_{3/2} set of excited states. Transitions such as these are well defined in energy; they are unique to the particular impurity or

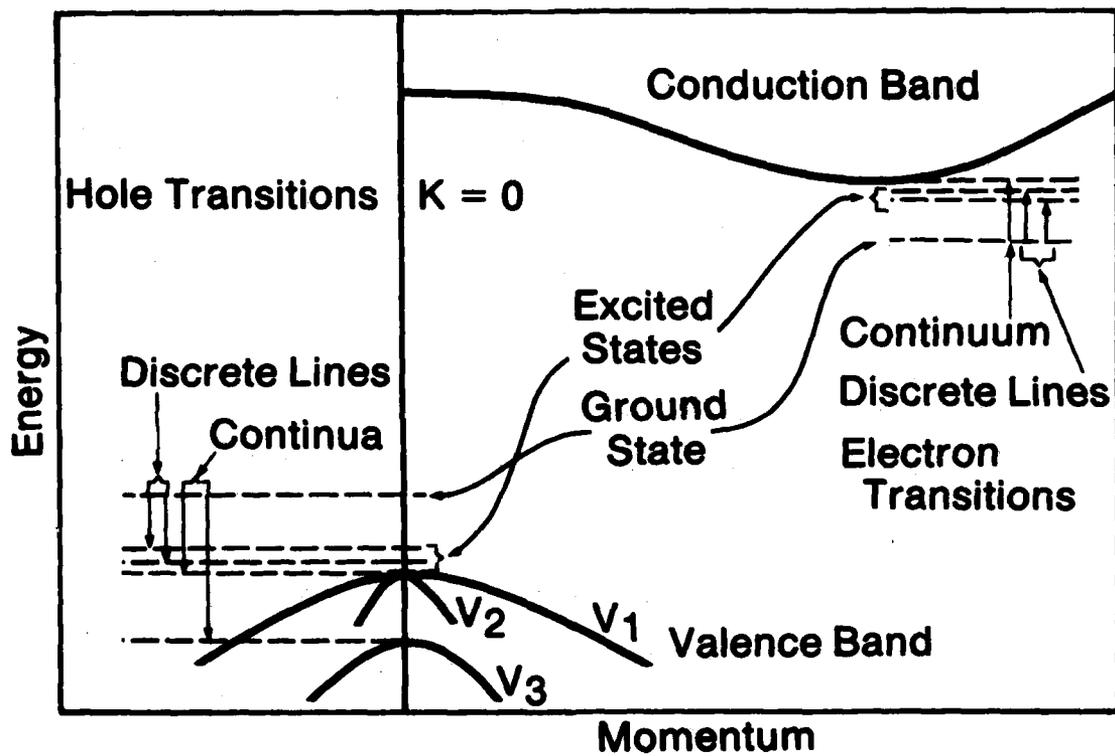


Figure 7. Bound states of n- and p-type impurities and possible electron and hole transitions

defect in a given semiconductor and can be used for both qualitative and quantitative analysis of impurities.

The spectrum shown in Figure 8 was measured at liquid He temperatures using a Digilab FTS-14 Fourier transform spectrometer. This instrument gives us the capability to rapidly and accurately quantitatively measure and identify impurities in semiconductors. This instrument offers us the advantage of

- o Spectral resolution of 0.5 cm^{-1} over its entire operating range.
- o Operational range of $10,000 \text{ cm}^{-1}$ (1 micron) to 20 cm^{-1} (500 microns).
- o Computer control of all operations.
- o Digital data handling and storage for data processing before display.
- o Software systems for operations on spectra, such as the subtraction of spectra.
- o Greater intensity throughout than dispersive spectrometers.
- o No stray light to give spurious results typical of dispersive spectrometers.

The samples are cooled to liquid He temperatures using an Air Products Heli-Tran cryostat equipped with suitably transparent windows. The energy

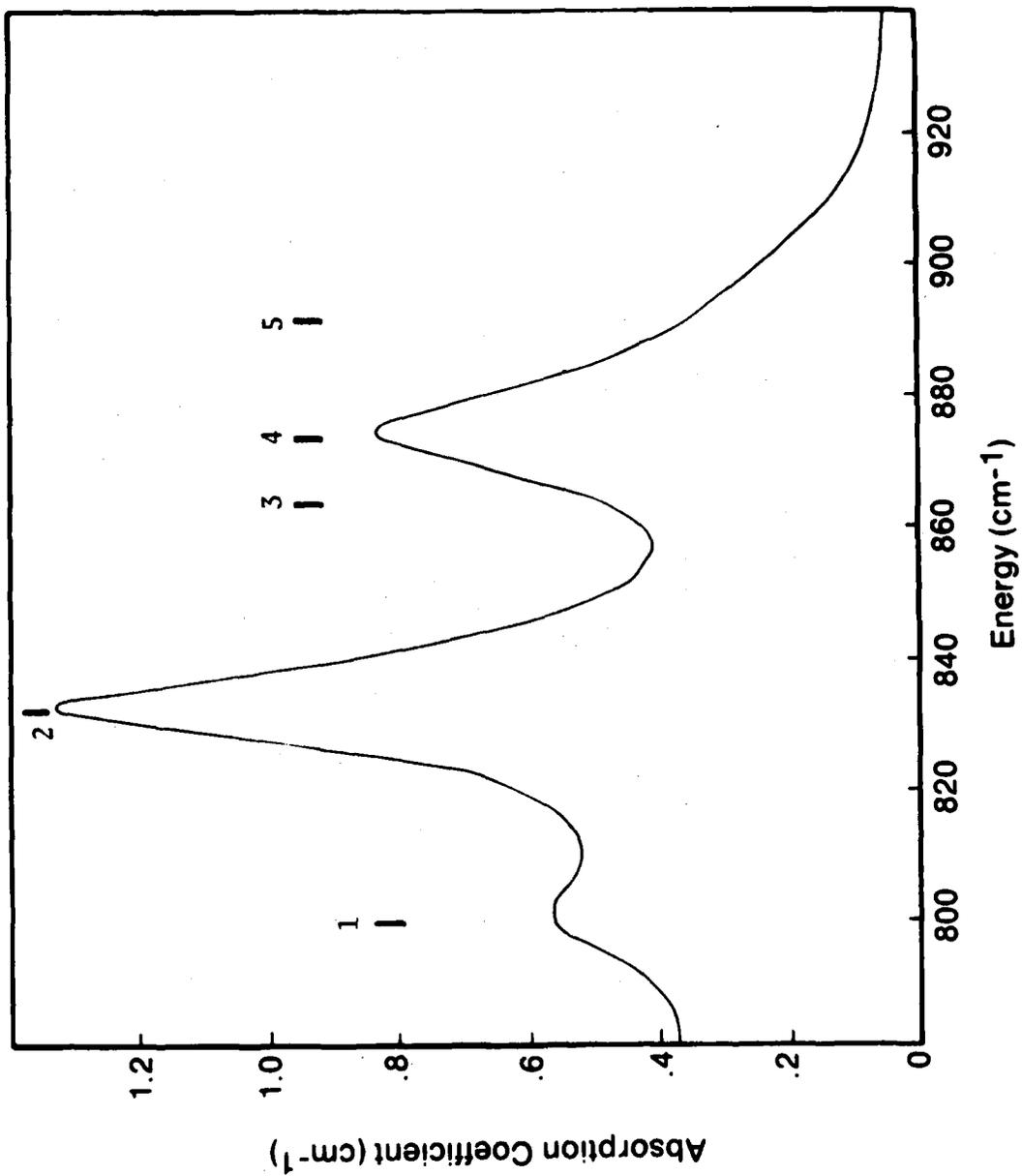


Figure 8. Infrared absorption spectrum of a silicon sample (SINX2 after 2 hours at 650C) containing 3.5×10^{15} In-X cm⁻³.

transmitted by the sample is measured and ratioed to the cryostat system without the sample. The sample and reference energy spectra are measured sequentially, so that the transmittance accuracy is limited by the stability of the spectrometer and by the accuracy with which the cryostat can be repositioned between measurements. The reproducibility is generally better than to within 5%. In cases where the impurity spectrum lies in a range including silicon lattice absorption, as is the case for the In-X spectrum, the absorption spectrum of a float-zone purity reference sample is subtracted from that of the sample to be measured.

Two impurities in silicon which are important to this work but whose IR spectra are not due to electrical excitation are oxygen and carbon. The absorption spectrum of silicon at liquid helium temperature in the 400 to 1600 cm^{-1} spectral region is shown in Figure 9. While most of the absorption in this region is due to the silicon lattice the line at 1136 cm^{-1} is due to a local vibrational mode of oxygen and the line at 607 cm^{-1} is similarly due to carbon. The 607 cm^{-1} carbon line is masked by a strong lattice line at 610 cm^{-1} so that the large peak at this energy is not all due to carbon. A unique capability of the FTS-14 system is its ability to subtract spectra from different samples and display only the difference. Using a float zone reference sample (which is for measurement purposes O and C free) the silicon lattice lines may be subtracted out leaving just the spectrum due to the added impurities in the test sample. This is shown also in Figure 8.

The intensity of the spectral lines of various impurities in silicon has been correlated to their concentration in silicon and is given in Table 3 for a

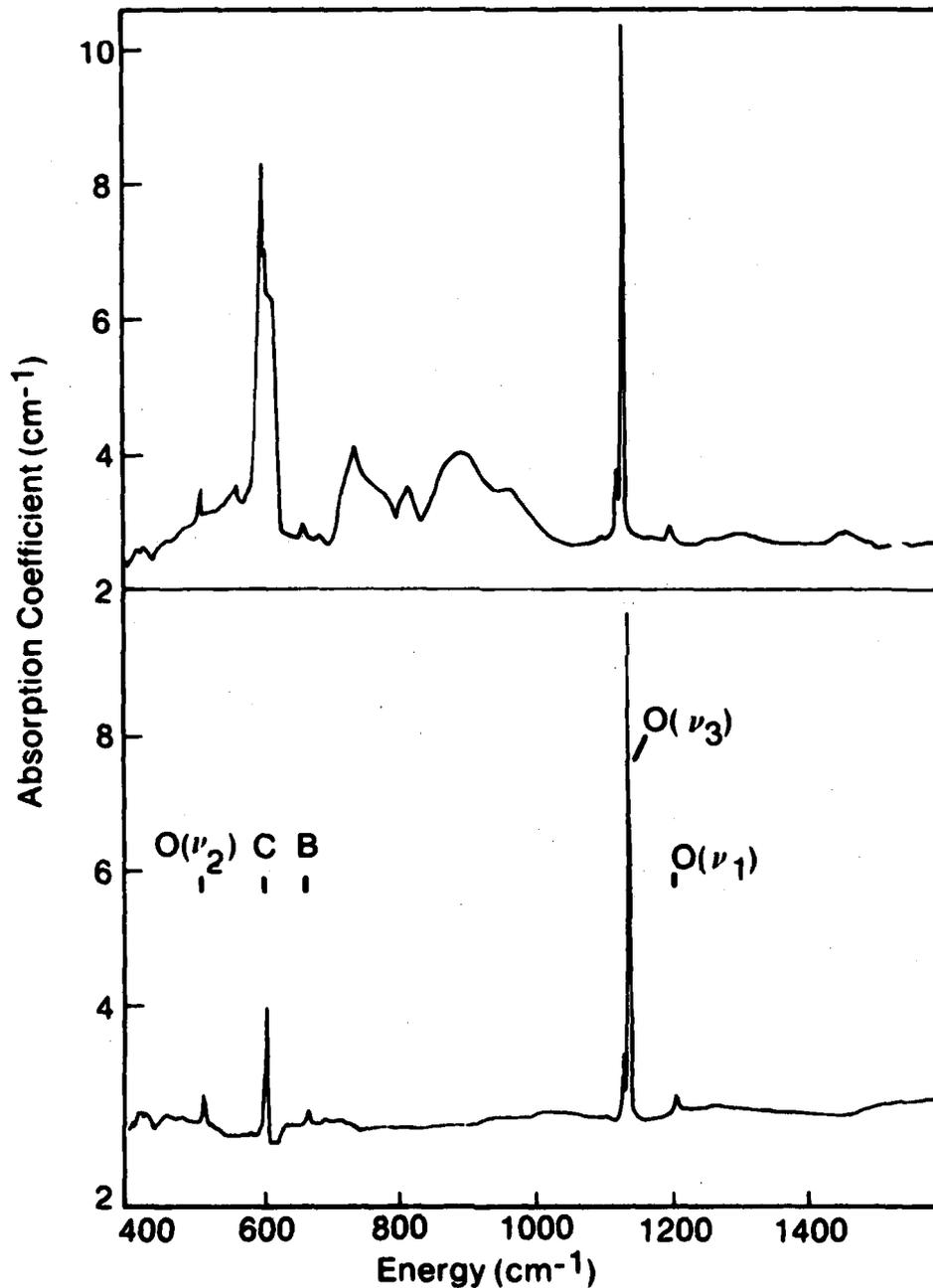


Figure 9. The absorption spectrum silicon at liquid helium temperature. The upper plot shows the spectrum due to impurities in the silicon and to the silicon lattice. The bottom plot shows the same spectrum with the structure due to the silicon lattice subtracted out thus revealing the spectra arising from the impurities. Note the three oxygen modes.

temperature of 8K. This conversion table will be used in our assessment of the presence of various impurities in our grown material.

TABLE 3. OPTICAL CALIBRATION FACTORS AT 8K

<u>Impurity</u>	<u>Line (cm⁻¹)</u>	<u>Concentration (cm⁻³)</u>
Boron	666	[B] = peak ^a x 1.66x10 ¹⁴
Aluminum (#2)	472	[Al] = area ^b x 4.17x10 ¹³
	(#1) 443	[Al] = area x 1.42x10 ¹⁴
Indium	1175	[In] = area x 2x10 ¹⁵
Carbon	607.5	[C] = peak x 6.7x10 ¹⁶
Oxygen	1136	[O] = peak x 3.09x10 ¹⁶
In-X	830	[In-x] = area x 2.86x10 ¹⁴
Al-X (#4)	414	[Al-x] = area x 3.4x10 ¹³

a) α peak = absorption coefficient in cm⁻¹ of absorption line

b) area = Area in cm⁻² of the absorption line

E. Hall Measurements

While infrared absorption was the primary measurement technique used in the analysis of our grown and heat treated material, Hall effect measurements were also conducted to help clarify experimental uncertainties. These measurements were done primarily on the Si(In, Al, C) system where the In-X concentrations were below the measurable limits of the FTIS spectrometer.

The Hall (and resistivity) measurements were made in a dc Hall system at a field of 8 kilogauss. The system has guarded leads which allow measurements of resistance as high as 10^{12} ohms. Because of the guarded lead arrangement the effective lead capacitance is < 10 pf, which is the input capacitance of the unity gain operational amplifiers used in the system. As a result, the RC time constants remain small. To adequately measure the Hall coefficient at these high resistances the temperature is automatically controlled with a Lake Shore Cryotronic Model DTC-500 temperature controller, which can control to within 0.02K over the range 300K to 4.2K. The Hall coefficient typically can be measured over ten orders of magnitude which gives an indication of the tremendous dynamic range of our system.

For Hall data which clearly result from more than one impurity level, a straightforward analysis can be carried out with the aid of a computer program which generates a theoretical Hall curve for a given set of impurity levels whose activation energies and concentrations have been specified. The activation energies of common impurities are known accurately from optical measurements, so that the problem is reduced to a choice of which impurities are present and what their concentrations are. The numerical approach to generating the theoretical Hall curve is quite general and consists of computing at each temperature the number of ionized donors and acceptors as well as the density of free holes or electrons, and adjusting the Fermi energy until the condition of charge neutrality is satisfied. Then the resulting carrier concentration is converted to a Hall coefficient value and compared with the data. The impurity concentrations put into the program are adjusted until the best fit of the theoretical curve to the data is obtained.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Growth of Si(In,C)

As mentioned in the introduction, a major goal of this program was to achieve In-X doping in the range of $5-10 \times 10^{16} \text{ cm}^{-3}$. This goal demanded a growth technique which allowed for maximum doping of Si with In and C. We adopted, therefore, the gradient transport solution growth method to provide for maximum In concentrations.

The Si(In,C) solution growth runs reported here were carried out in the range of 1200C to 1340C. The temperature of the furnace was ramped up slowly ($\leq 100\text{C/hr}$) to the growth temperature after which the graphite gradient heater was turned on. Typical temperature gradients across the solution layer were approximately 5C/cm which allowed for growth rates in the order of 1mm/day. All growth runs were carried out under an argon gas ambient.

Five solution growth runs were carried out during the course of this contract, all of which followed the above prescription. Of these five, three resulted in producing adequate material for annealing studies, etc. The solution layer of the other two runs broke up during growth resulting in small droplets of In migrating non-uniformly along the growth axis. This material was not analyzed further. The material from the three successful growth runs was then prepared for optical and Hall measurements.

B. Annealing Studies of Si(In,C)

In order to maximize the In-X concentration in Si(In,C) the material must be annealed for a suitable period of time at low temperatures. In the first part of this report it was determined that if In and C concentrations were near the maximum solubility limits in Si then annealing temperatures of the order of 550C would be adequate to achieve In-X concentrations in the mid 10^{16}cm^{-3} range. Our objective in this study then is to determine if these concentrations can be achieved and to get a handle on the reaction kinetics of In-X formation at these temperatures.

The material from the first growth run (SINX1) was subjected to several heat treatments at 550C. After each anneal the sample was chemically cleaned and then cooled to 8K for transmittance measurements on the Digilab FTS-14 spectrometer. The transmittance was measured at a resolution of 2 cm^{-1} and then converted to the absorption coefficient in the usual way. The absorption lines due to In, C, O and In-X were monitored after each treatment. The optical calibration factors for these lines are given in Table 3. A 20,000 $\Omega\text{-cm}$ float zone silicon reference spectrum was used to subtract off the silicon lattice lines.

The concentrations of In, C, O, and In-X levels are given in Table 4 for SINX1 after each of the heat treatments at 550C. Using the In and C concentration as measured after the 21 hour anneal the expected In-X equilibrium concentration at 550C is $7 \times 10^{15}\text{cm}^{-3}$ according to Equation (1). Obviously, equilibrium was not established after the 21 hour anneal.

TABLE 4. IMPURITY CONCENTRATION LEVELS (cm^{-3}) IN SAMPLE
SINX1 AFTER HEAT TREATMENTS AT 550C

550C Anneal for	21 hrs.	37 hrs.	65 hrs.	90 hrs.	176 hrs.
[In]	6.9×10^{17}	7.1×10^{17}	7.4×10^{17}	7.1×10^{17}	7.4×10^{17}
[C]	1.1×10^{17}	1.1×10^{17}	8.5×10^{16}	7.4×10^{16}	3.8×10^{16}
[In-X]	1.8×10^{15}	2.7×10^{15}	2.8×10^{15}	2.9×10^{15}	1.8×10^{15}
[O]	3.2×10^{17}	3.3×10^{17}	3.3×10^{17}	3.1×10^{17}	2.6×10^{17}

The subsequent anneals of SINX1 at 550C were done to study the reaction kinetics of the In-X center as equilibrium is approached. The In-X concentrations of SINX1 versus annealing time is plotted in Figure 10. It is apparent from this figure and Table 3 that the concentration of In-X centers does not approach its expected equilibrium value at 550C. Concurrent with this leveling off and then decrease of In-X centers is the significant reduction in carbon concentration. The amount of carbon is reduced by almost an order of magnitude after 176 hours of annealing.

It was thought initially that the decrease in In-X and C concentrations was due somehow to the numerous thermal cyclings of the material. Perhaps the thermal cycling introduced defects in the material at which the In-X or C would precipitate out. To determine if thermal cycling played a role in the elimination of In-X centers in Si, material from the second solution growth run (SINX2) was prepared for a long term anneal. First the sample was

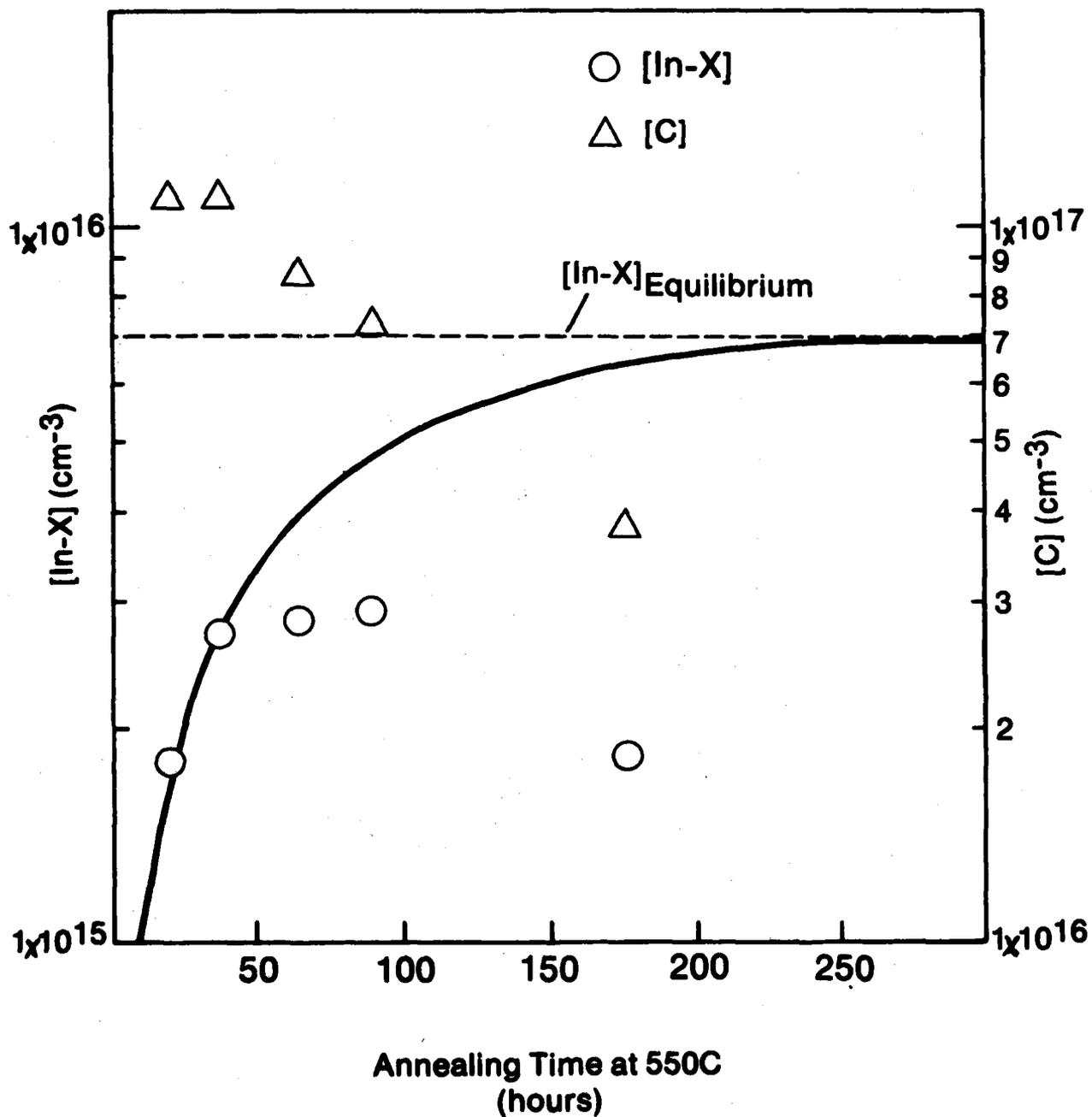


Figure 10. Annealing data for sample SINX1 at 550C showing the concentration of In-X and C as a function of annealing time. The solid line describes the expected increase of In-X centers versus time assuming that at long annealing times the equilibrium value of [In-X] is reached.

annealed for two hours at 650C after which its absorption spectrum was measured. This was done to establish the baseline concentrations of In, C, and In-X. From these concentrations it was estimated from Equation (1) that an anneal at 500C was necessary to achieve mid 10^{16} cm^{-3} of In-X centers. Consequently sample SINX2 was annealed for 353 hours at 500C. The results of this anneal are given in Table 5. The C concentration decreased by an order of magnitude and the In-X concentration was below our detectable limits. A 20 hour anneal at 650C was performed subsequently to determine if these losses were reversible. Note the continued reduction in C concentration after the 20 hour anneal.

TABLE 5. IMPURITY CONCENTRATION LEVELS (cm^{-3}) IN
SAMPLE SINX2 AFTER VARIOUS HEAT TREATMENTS

	2 hr. at 650C	353 hr. at 500C	20 hr. at 650C
[In]	7.3×10^{17}	4.7×10^{17}	5.8×10^{17}
[C]	2.2×10^{17}	2.1×10^{16}	$< 3.5 \times 10^{15}$
[In-X]	3.5×10^{15}	$< 1.0 \times 10^{14}$	$< 1.0 \times 10^{14}$
[O]	3.9×10^{17}	1.0×10^{17}	1.2×10^{17}

The results of these two sets of anneals imply that some type of reaction(s) is (are) competing with the In-X formation at low annealing temperatures and long annealing times. The concentration of In-X centers decreases

dramatically for long term anneals in the 500-550C temperature region. Concurrent with this decrease is the loss of significant amounts of C. Because of carbon's assumed role in the In-X complex we must understand its reduction during long term heat treatments in order to explain the loss of In-X.

The reduction of carbon in heat treated silicon samples has been observed in numerous investigations.¹³⁻¹⁸ This reduction has been attributed to the formation of carbon-oxygen (C-O) complexes and to the formation of SiC microprecipitates. C-O complexing in silicon was determined by the appearance of satellite lines near the carbon and oxygen fundamentals and the simultaneous reduction in intensity of the fundamentals themselves. The evidence for SiC precipitation is shown by the presence of a broad symmetric band with peak absorption at about 835 cm^{-1} which is in the same spectral region as the In-X lines. For the case of SiC precipitation it was found that precipitation occurs only in pulled (i.e., Czochralski grown) crystals which also contained substantial amounts of oxygen.

We have investigated the absorption spectra of our heat treated samples to determine if C-O complexing or SiC precipitation has occurred. For C-O complexes this is difficult because of the relatively weak line intensities expected. The strongest of the C-O satellites is the O satellite at 1104 cm^{-1} (measured at 4.2K). Newman and Smith¹³ measured an integrated intensity for this line of 3.4 cm^{-2} for a sample doped with $1.6 \times 10^{18}\text{ cm}^{-3}$ and $1 \times 10^{18}\text{ cm}^{-3}$ carbon and oxygen respectively. Since the C and O concentrations of our samples are much less, the intensity of the line at 1104 cm^{-1} is anticipated

to be much less also.

We have found evidence, however, for C-O complexing in our samples. Figure 11 shows the absorption spectra for sample SINK1 in the region of 1104 cm^{-1} after each of the 550C heat treatments. Note the increase in intensity of this line after the third (65 hour) anneal. This occurs at the same time that the C and In-X concentrations begin to decrease.

The integrated intensity expected from silicon carbide precipitates can be estimated from a theory which describes the infrared absorption by small diameter (1-10 micron) particles embedded in a matrix of high dielectric constant. This theory is reviewed by Ruppin and Englman¹⁹ and applied to SiC precipitates in silicon by Bean and Newman.¹⁵ Bean and Newman were able to calculate both SiC line position and line intensity by assuming that the measured loss of C in the sample was due entirely to precipitation. Their results compared favorably with experiment. Using our experimentally determined values for the loss of C we can estimate what the integrated intensity due to SiC microprecipitates will be. This integrated intensity is of the order of 10 cm^{-2} with a peak absorption in the region of $835\text{--}840\text{ cm}^{-1}$. Figure 12 shows the absorption spectra in this region for sample SINK2. Note the dramatic reduction in intensity of the In-X lines and the emergence of a broad peak in the $835\text{--}840\text{ cm}^{-1}$ region. The measured intensity of this peak is $\sim 4.5\text{ cm}^{-2}$ which agrees fairly well with that estimated. If we had assumed that not all of the measured loss of C precipitated in the form of SiC, the difference between the calculated and measured values would be even less. The remainder of the lost C would likely form C-O complexes.

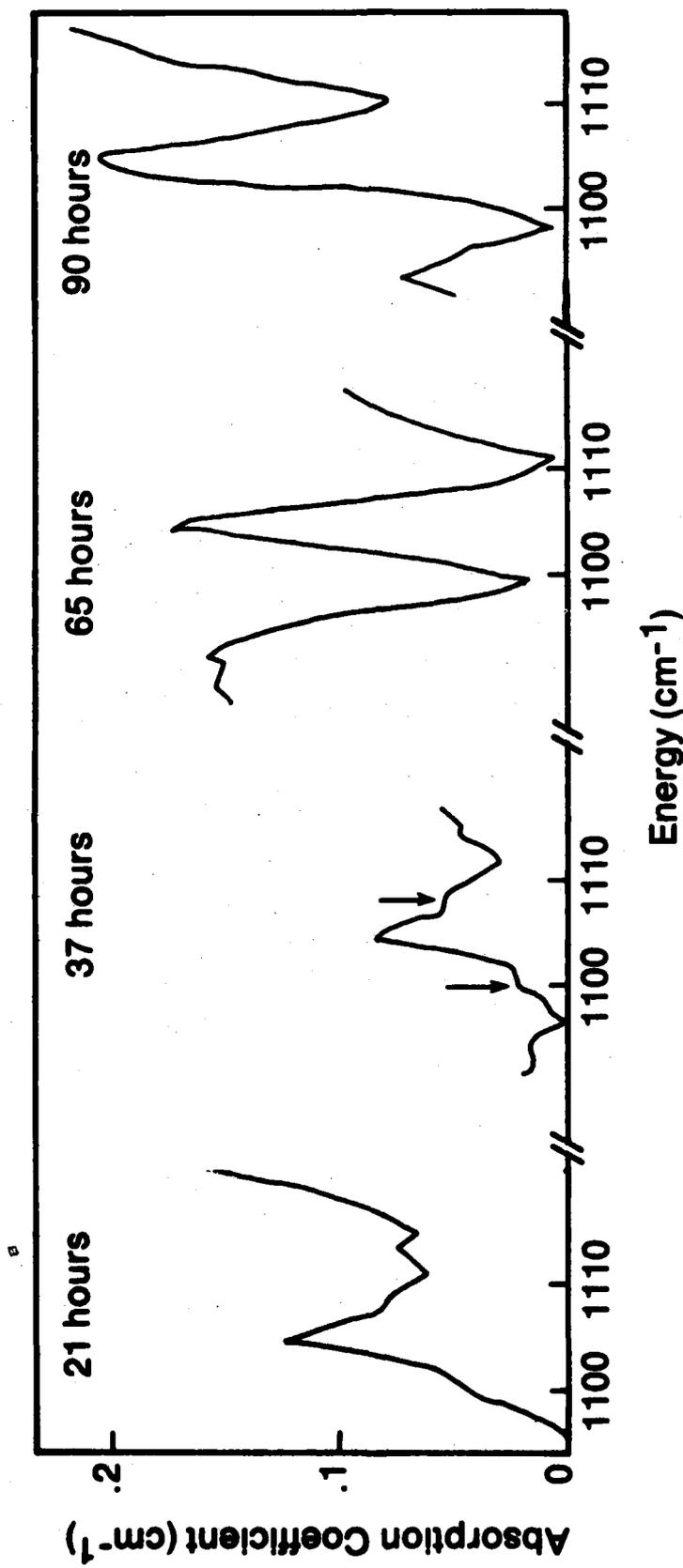


Figure 11. The spectrum for sample SINX1 in the region of 1100 cm^{-1} showing the absorption due to C-O complexing. Absorption due to the silicon lattice has been subtracted off.

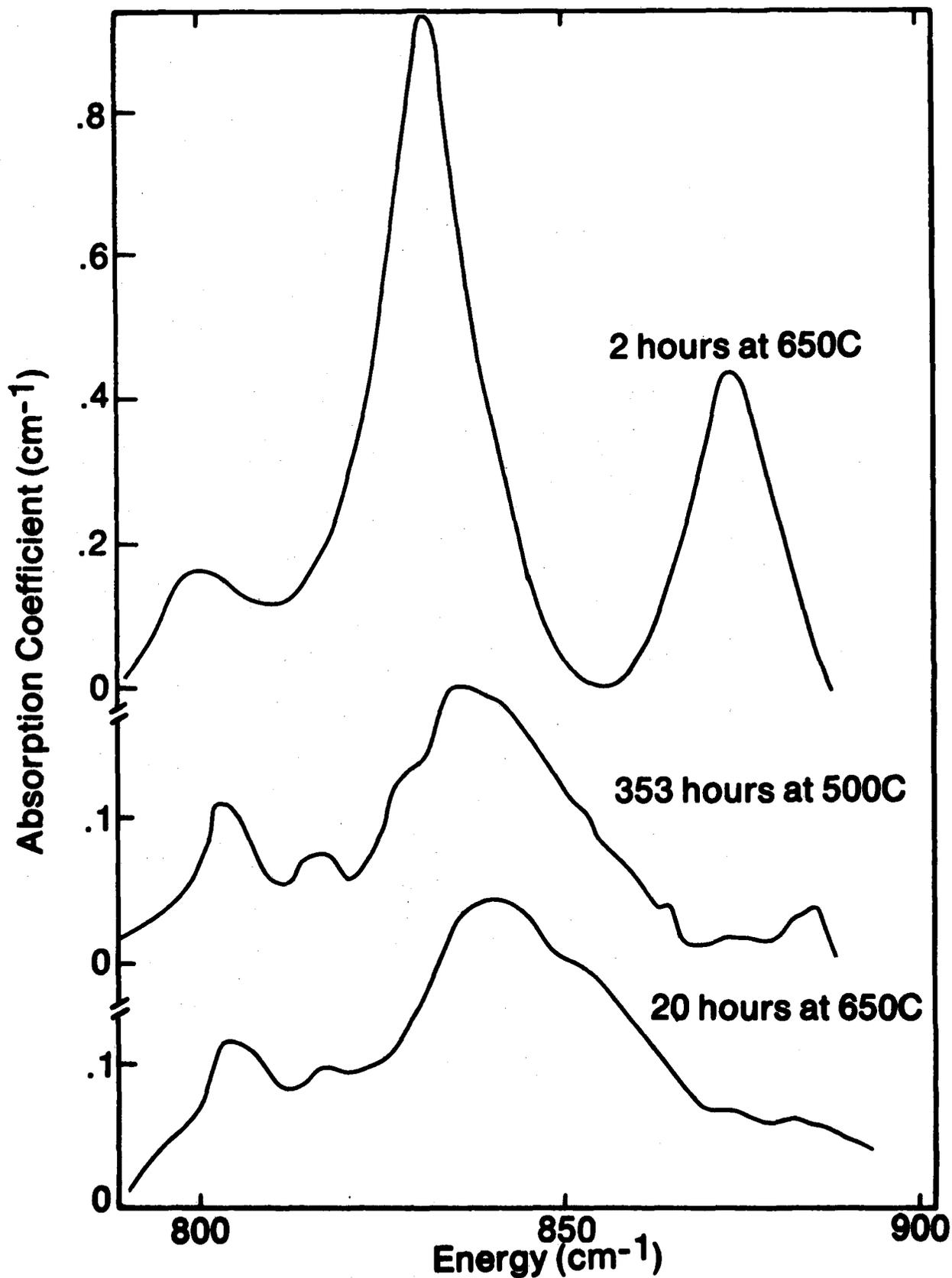


Figure 12. Absorption in the region of the In-X lines after anneals of sample SINX2. Absorption due to the silicon lattice has been subtracted off.

We have explained the loss of C in our heat treated Si(In,C) samples by the simultaneous formation of SiC precipitates and of C-O complexes. While these two mechanisms of C loss do not preclude other processes, they are consistent with other investigations of C loss in silicon. We believe then that these are the predominant mechanisms involved.

It was mentioned previously that SiC precipitation was observed only in materials with significant oxygen concentrations. Bean and Newman¹⁵ speculated that oxygen in silicon precipitates onto vacancy clusters and these "particles" then act as nuclei for the growth of silicon carbide particles. Coupled with the observation of C-O complexes it would appear that oxygen is playing an inhibiting role in the formation of the In-X complex at low temperatures. Thus, to achieve In-X concentration suitable for efficient photoconductors the oxygen content of Si(In,C) crystals must be reduced. This may have serious consequences since it has been suggested that the presence of oxygen enhances the diffusion of C in silicon. Eliminating the oxygen from the material may slow the reaction kinetics of the In-X formation to an unacceptable rate. Previous studies^{20,21} of Si(In) using float zone silicon as starting material found that for temperatures greater than 600C much longer annealing times were necessary to achieve equilibrium concentrations of In-X centers.

We have made several attempts to grow O free Si(In,C) crystals so as to measure and clarify the above mentioned effects. Float zone starting material was used for the source and substrate while high purity carbon was added by

sprinkling it over the indium solution prior to growth. The growth runs were then carried out as described previously. However, we were unable to obtain any "oxygen-free" material from these growth runs. We speculate that the presence of large carbon particles in the thin solution layer caused this layer to break up during growth.

C. Studies of Si(In,Al)

The second objective of this work was to investigate the effects of Al on In-X formation. As mentioned previously it has been suggested⁶ that the In-X defect is an Al-In complex stabilized by the presence of C. If this is indeed the case, then the addition of Al to In doped silicon should enhance the In-X concentration.

We have grown Si(In,Al) single crystals by the Czochralski method to study the effects of Al on the In-X center. An ingot 8 inches long was grown from a (111) oriented silicon seed dipped into a Si-In-Al melt. Thus, the grown boule was of (111) orientation of which about one half was single crystalline. The single crystalline section of the boule was separated and wafered for optical measurements and annealing studies.

Prior to any anneals, one of the wafers was analyzed on the FTS spectrometer to determine impurity content. In,Al and C concentrations were 5, 2.5 and $21 \times 10^{16} \text{cm}^{-3}$ respectively. From the law of mass action, Equation (1), an estimated value for the expected In-X (or Al-X) concentration can then be determined for any annealing temperature. These values can be determined from

Figure 1.

Subsequently, Si(In,Al) wafers were annealed at 650C, 750C, 850C and 950C with their absorption spectrum being determined after each anneal. Since the absorption spectrum was measured in the energy range of 400 cm^{-1} to 4000 cm^{-1} , the Al-X concentration was determined from the Al-X #4 line instead of its #2 line.³ This was done by correlating the intensities of the #2 and #4 lines for a number of Si(Al) samples investigated previously.³ Also, because the absorption by Al is relatively high, it was necessary to use the Al #1 line instead of the Al #2 line to determine its concentration. The procedure to do this was the same as for the Al-X line. These conversion factors are given in Table 1.

The results of the various anneals are given in Table 6 along with the expected In-X and Al-X concentrations from Equation (1) (most measurements were made on different sections of the same wafer to ensure minimum variation in In, Al and C contents). Note the measured In-X concentration as compared to what is expected. Even after the long term anneal at 650C, the measured In-X concentration does not approach its equilibrium value. It would appear that not only does the presence of Al not enhance In-X formation, but it actually suppresses it. Figure 13 compares the spectrum in the In-X region of sample 2D after one hour at 750C with the spectrum of a Si(In) sample comparably doped and annealed at the same temperature for the same time. The In-X line in the Si(In,Al) sample is barely detectable. Analysis of the Hall data on these Si(In,Al) samples using a fitting program to determine impurity concentrations did not show any presence of In-X centers. These observations

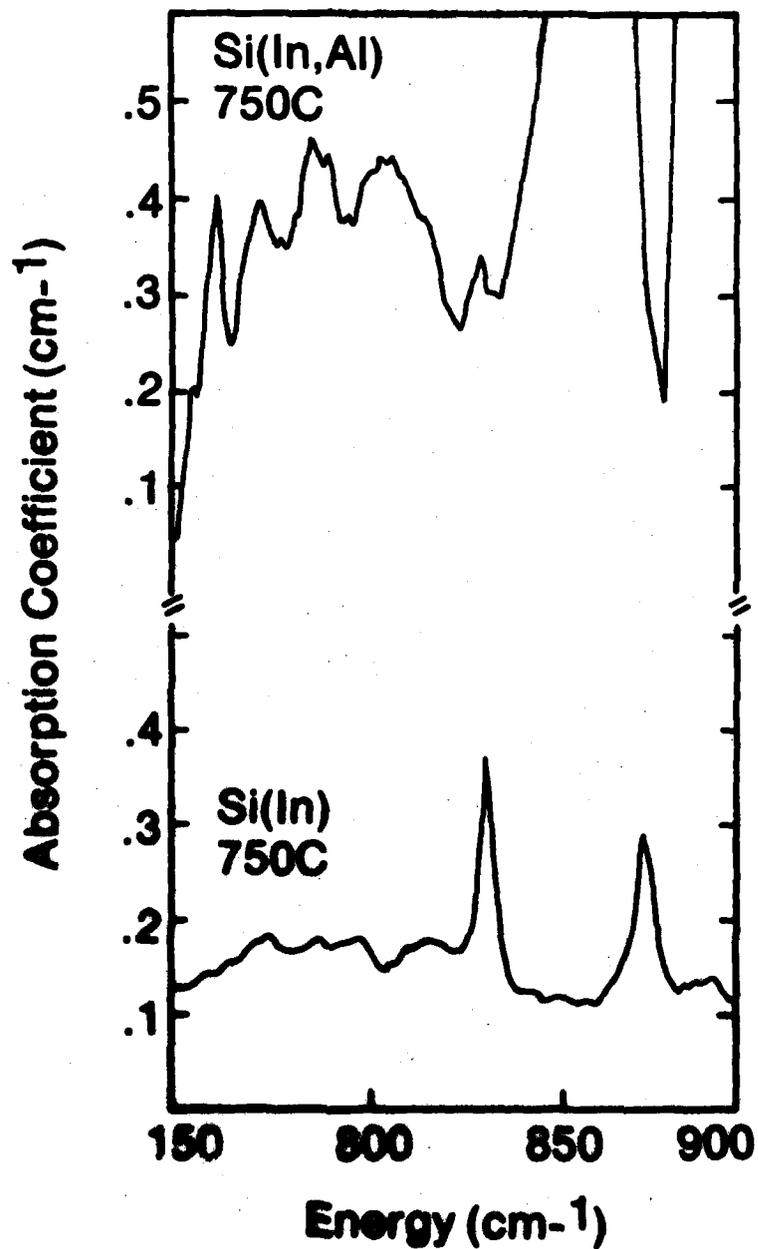


Figure 13. Absorption in the region of the In-X lines in a Si(In,Al) sample and a Si(In) sample both of which are comparably doped with In and C and annealed for one hour at 750C. The strong absorption in the Si(In,Al) sample at 850 cm⁻¹ is due to the Al 2p' excited state.

coupled with the results of the Si(In,C) anneals lends more credence to the belief that the In-X defect is an In-C complex.

TABLE 6. Impurity Concentrations of Si(In,Al) Samples After Various Heat Treatments. The Expected In-X and Al-X Concentrations are Calculated from Equation (1) Using the Measured In,C, and Al Concentrations.

	Sample 2E 1 hrs. @650C	2E 64 hrs. @ 650C	2D 1 hrs. @ 750C	2F 1 hrs. @ 850C	2I 1 hrs. @ 850C
[C]	$2.1 \times 10^{17} \text{ cm}^{-3}$	1.3×10^{16}	2.0×10^{17}	1.7×10^{17}	2.1×10^{17}
[B]			2.9×10^{14}	2.1×10^{14}	2.5×10^{14}
[In]	5.0×10^{16}	5.0×10^{16}	5.0×10^{16}	4.6×10^{16}	4.4×10^{16}
[In-X]	$< 5.0 \times 10^{13}$	$< 5.0 \times 10^{13}$	$< 5.0 \times 10^{13}$	$< 5.0 \times 10^{13}$	$< 5.0 \times 10^{13}$
[In-X] expected	2.7×10^{14}		1.1×10^{14}	4.2×10^{13}	2.8×10^{13}
[Al]	2.4×10^{16}	3.9×10^{15}	2.4×10^{16}	2.8×10^{16}	2.2×10^{16}
[Al-X]	2.6×10^{14}	$< 1.0 \times 10^{13}$	4.5×10^{14}	1.6×10^{14}	7.8×10^{13}
[Al-X] expected	6.7×10^{14}		4.9×10^{14}	2.9×10^{14}	3.3×10^{14}

Accomplishments and Conclusions

During this program we have shown that there are competing reactions to the formation of the In-X center and that the presence of Al does not enhance the concentration of In-X. Specifically we find evidence for the formation of C-O complexes and SiC precipitation in low temperature heat treated Si(In,C) samples. These reactions tie up C atoms which could be available for In-X complexing. Accordingly, the law of mass action shows that a reduction in available C leads to smaller In-X concentrations. The C-O complexing and SiC

precipitation is thought to be related to the presence of oxygen in the sample. However, previous studies of O free Si(In) find the reaction kinetics of the In-X formation to be extremely slow. Thus to achieve mid 10^{16} cm^{-3} of In-X may take prohibitively long annealing times.

We also find that large concentrations of Al suppress the formation of In-X centers, contrary to the theory that the In-X center is an In-Al complex. This result thus eliminates most of the objection remaining to the In-X center being an In-X complex.

In summary, we conclude that the In-X center in silicon does not offer a viable choice as an active level in a photoconductor. The stringent material requirements and the competing reactions to In-X formation make concentrations of In-X in the mid 10^{16} cm^{-3} range all but impossible to achieve.

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