Infrared spectroscopy of silicon for applications in astronomy

B. Uzakbaiuly and D. B. Tanner
Department of Physics, University of Florida, Gainesville, FL 32611-8440, USA

J. Ge
Department of Astronomy, University of Florida, Gainesville, FL 32611-8440, USA

J. Degallaix
Albert-Einstein-Institut, Max-Planck-Institut für Gravitationsphysik, D-30167 Hannover, Germany

A. S. Markosyan
Stanford University, Stanford, CA 94305, USA

(Dated: August 21, 2018)

This work focuses on the characterization of various bulk silicon (Si) samples using Fourier Transform InfraRed (FTIR) and grating spectrometers in order to get them suitable for applications in astronomy. Different samples at different impurity concentrations were characterized by measuring their transmittance in the infrared region. Various lines due to residual impurity absorption were identified and temperature dependence of impurity absorption is presented. Concentrations of doped samples ($\rho \approx 0.2 - 25000 \Omega \text{cm}$) were determined from impurity absorption at low temperatures and from Drude free carrier absorption at 300K.

I. INTRODUCTION

This work is based upon characterization of silicon (Si) for astrophysical applications. Two proposed applications motivate this work. One is the use of silicon immersion gratings (SIGs) in future infrared spectrometers for satellite telescopes. Immersion grating technology has emerged as an alternative for conventional echelle grating technology in applications where size and weight are important. Instead of having incident light reflected and diffracted from the front surface of a conventional diffraction grating, the immersion grating prior light is transmitted into the medium. Diffraction occurs at the back surface. The wavelength of the light inside of the grating is reduced by refractive index of the medium. So the resolution and dispersion are going to be increased by same amount. Since Si has refractive index of 3.4, SIGs offer 3.4 times gain in spectral resolution over conventional echelle gratings of the same length and blaze angle. This gain can also be viewed as a 10 times reduction in the instrument size, meaning that the instrument would weight less and be more suitable for space or airborne applications. SIGs have silicon (Si) as the host material, relying on its high transparency in much of the infrared region.

Si is transparent below the multiphonon absorption for far infrared (10 - 600 cm$^{-1}$) use as well as in the near infrared (2000 - 9000 cm$^{-1}$). However, in the far infrared, narrow lines due to residual impurities appear at low temperatures. These will play a significant role in the performance of SIGs and characterization of high purity of Si is required for optimal operation conditions.

A second application is related to incorporating Si in next generation telescopes and detectors. Cryogenic operations are expected to produce substantial improvements in the performance of gravitational-wave detectors. The required position accuracy of the test masses in future detectors is in the range of $10^{-21}$ m or better. Achieving this precision will require improvements over current technologies in many areas, including the massive substrates for the interferometer test masses. KAGRA, a 3 km underground gravitational-wave detector and the proposed European Einstein Telescope (ET) are exploring cryogenic operations of gravitational-wave detectors, but significant technological hurdles remain. It is important first to select a mirror substrate compatible with cryogenic operation. The material must have good optical qualities, high thermal conductivity, low thermoelastic coefficient, and be available as large, high quality single crystals. KAGRA has selected sapphire for the cryogenic test masses, whereas the ET design is based on the use of silicon. Owing to its technological importance, silicon has been studied in great detail. Crystals as large as 40 cm diameter, 1.1 m in length and weighing more than 425 kg have been produced. The semiconductor industry routinely cuts and polishes these crystals into wafers up to 30 cm in diameter; development of 45 cm diameter materials is continuing with research being conducted in the US, Europe, and Japan. Silicon has already met the mass goals for the test masses of future gravitational-wave detectors. Suspensions for a cryogenic silicon test masses have been designed and studies are in progress.

Test masses require low absorption coefficients to provide high transmissive throughput and minimize thermal distortions. Homogeneous optical properties are also required. Optical absorption in substrates results in significant changes in the radii of curvature of the mirror surfaces (due to thermal expansion) and the focal power of the substrates (due to thermal lensing), chang-
ing the fundamental arm cavity mode structure. Silicon operating at cryogenic temperatures is a particularly strong candidate for third-generation detector test masses. In some experiments, absorption falls below $10^{-7}$ cm$^{-1}$, 10 times lower than absorption in fused silica at 1064 nm. However, other experiments show considerably higher absorption.

A. Hydrogen-Like Impurity States in Si

There have been numerous experimental and theoretical studies to investigate donor or acceptor defects appearing in Si lattice. Most of them use a picture where an electron or a hole at the impurity is assumed to be in the screened Coulomb potential of the ion core. This screening is due to the dielectric constant of the host atom, Si. The effective mass of the carriers in the Si band structure plays a role as well. The problem of a group VI/IV donor/acceptor atoms in group V Si is very similar to the hydrogen atom problem in quantum mechanics because the extra electron/hole of the donor can be assumed to be influenced by the Coulomb potential screened by a dielectric constant $\epsilon$. The Hamiltonian can be formally written as

$$\mathcal{H}_{EM} = -\frac{\hbar^2}{2m^*} \nabla^2 - \frac{e^2}{4\pi \varepsilon_0 \varepsilon_a r}.$$  \hspace{1cm} (1)

The energies of this particle would be just the Rydberg energies of hydrogen atom modified by the effective mass ($m^*$) and dielectric constant $\epsilon$ if the conduction/valence band were described by simple quadratic formula. However, the conduction band minimum, as well as the valence band maximum, is complex which requires a rigorous approach to solve for donor/acceptor excited states.

The conduction band minimum which is located close to the X symmetry point of the Brillouin zone has six symmetry points and the constant energy surfaces in k-space can be described by prolate ellipsoids of revolution. This anisotropy of constant energy surfaces causes the effective mass to be anisotropic: a longitudinal mass along the main axis of the ellipsoid ($m_\parallel = 0.92m$) and a transverse mass perpendicular to the main axis ($m_\perp = 0.19m$). This anisotropy also plays a factor in electrical conductivity effective mass. The valence band maximum for Si crystal is at the $\Gamma$ point and has two types of energy dispersions. The one with a smaller energy dispersion has a larger mass $m_{hh} = 0.54m$, and the one with a higher energy dispersion has a lower mass $m_{th} = 0.15m$. These are fourfold degenerate $p_{3/2}$ like states whose constant energy surfaces are warped spheres in k-space. There are also twofold degenerate $p_{1/2}$ states which are separated from the former by an energy of $\Delta_0 = 0.042$ eV.

B. Oscillator Strength of Transitions from ground state

The oscillator strengths of the various transition lines for P donor impurity in Si have been calculated by Clauws et al. They assumed a Hamiltonian with a potential defined by

$$\frac{2}{r} \left[ 1 + (\epsilon_\infty - 1) e^{-\alpha' r} \right],$$  \hspace{1cm} (2)

where $\alpha'$ is a phenomenological parameter which changes according to the ground-state energy value. The wavefunctions of the above Hamiltonian are used to find the oscillator strength

$$f_{a \rightarrow b} = \frac{2m^*}{\hbar^2} (E_b - E_a) |\hat{\epsilon} \cdot \mathbf{r}_{ba}|^2,$$  \hspace{1cm} (3)

where $\hat{\epsilon}$ is the unit polarization vector of the radiation and $\mathbf{r}_{ba}$ is the dipole matrix element. This is an electric-dipole transition between state $a$ with energy $E_a$ and state $b$ with energy $E_b$ ($E_a < E_b$). In addition, the donor effective mass is given by equation

$$m^* = \frac{3m_\parallel m_\perp}{2m_\parallel + m_\perp}.$$  

The transition probabilities are normalized making $\sum_b f_{a \rightarrow b} = 1$. Calculated oscillator strengths are the transition strengths from 1s ($A_1$) ground state to higher states which is either to odd parity $m_l = 0$ or $m_l = \pm 1$.

Another authors (Ref. 13) also determined the oscillator strengths of the ground-state to higher-state transitions. Using the wave function for the Hamiltonian and a non-variational method, they arrive at the solution for the oscillator strengths

$$f(nP_0) = \frac{2\zeta}{2 + \zeta} \left[ E(nP_0) - E_0 \right] \times \sum_{l \geq 1} \int_0^\infty d\tilde{r} \tilde{r}^3 F_L^{(0)}(\tilde{r}) \tilde{R}_L^{(0)}(\tilde{r})^2,$$

$$f(nP_\pm) = \frac{4}{2 + \zeta} \left[ E(nP_\pm) - E_0 \right] \times \sum_{l \geq 1} \int_0^\infty d\tilde{r} \tilde{r}^3 F_L^{(1)}(\tilde{r}) \tilde{R}_L^{(1)}(\tilde{r})^2,$$  \hspace{1cm} (4)

where $R_L(\tilde{r})$ and $F_L^{(M)}(\tilde{r})$ stand for the radial wave function of the initial ground and final state respectively.
TABLE I. Calculated oscillator strength of shallow P donor transitions from the 1S(Γ4) state in Si

| Final state | Energy of transition for P | OS | OS |
|-------------|-----------------------------|----|----|
| 2P0         | 34.109(275.108) meV (cm⁻¹) | 0.0312 | 0.0313 |
| 2P±         | 39.175(319.966) meV (cm⁻¹) | 0.1325 | 0.133 |
| 3P0         | 40.104(322.566) meV (cm⁻¹) | 0.0064 | 0.00644 |
| 3P±         | 42.458(342.45) meV (cm⁻¹) | 0.030 | 0.0304 |
| 4P0         | 43.388(349.95) meV (cm⁻¹) | 0.0108 | 0.0108 |
| 5P±         | 44.119(355.84) meV (cm⁻¹) | 0.0088 | 0.00009 |

Table I lists the oscillator strengths for selected transition lines of phosphorus (P) impurity in the Si lattice as calculated by Clauws et al. and Beinikhes and Kogan. The overall pictures seem to agree with each other. As can be noted, the 1s(Γ4) → nP± transitions are stronger than 1s(Γ4) → nP0 ones. This is expected when considering multi-valley degeneracy and arbitrary choice of polarization vector. As for boron impurity in Si, the oscillator strengths have been calculated by Buczko and Bassani and Pajot et al. Buczko assumed same Coulomb potential of the negatively charged acceptor center as in Eq. 2 and used variational method to arrive at the oscillator strength derived from the Luttinger Hamiltonian. The oscillator strength for optical transitions, which should obey the sum rule, is

\[
f_{of} = \frac{2m^*_v}{\gamma_1 \hbar^2} \left[ E_f - E_0 \right] \sum_{i,j} \left| \langle \Phi_{0,i} | z | \Phi_{f,j} \rangle \right|^2, \quad (5)
\]

where \( \gamma_1 \) is Luttinger parameter and \( m^*_v \) is the conductivity effective mass for holes

\[
\frac{1}{m_v} = \frac{1}{m_{hh}^1 + m_{lh}^{1/2}} = \frac{1}{m_{hh}^1 + m_{lh}^{1/2}}.
\]

Calculated oscillator strengths are transitions from 1Γ8 ground state to excited states. Pajot et al. has calculated the oscillator strengths of transitions from ground state using a non variational method. Assuming acceptor-dependent ground state wavefunction, he arrived at electric dipole transition

\[
f(a \rightarrow b) = \frac{E_b - E_a}{g_0} \times \sum_{m,n} \left( \sum_{JFL} (-1)^{F - F_e} C_{mF_e} C_{nF_e} C_{mF_e} \right) \left\{ \begin{array}{ccc} F_n & 1 & F_b \\ -F_z & 0 & F_e \end{array} \right\} \times \left( L_a J_a F_a || | r | L_b J_b F_b \right)^2,
\]

where \( a \) and \( b \) denote two discrete states. The oscillator strength is normalized to unity which corresponds to sum of discrete as well as continuous transitions. Table II gives the OS of transitions from ground state 1Γ8 to the indicated excited state transition in B doped Si.

TABLE II. Calculated oscillator strength of shallow B acceptor transitions from the 1Γ8 state in Si

| Final state | Energy of transition for B | OS \( \times 10^{-4} \) | OS \( \times 10^{-4} \) |
|-------------|-----------------------------|------------------|------------------|
| 1Γ8         | 30.3694(244.946) meV (cm⁻¹) | 194 | 177 |
| 2Γ8         | 34.5042(278.295) meV (cm⁻¹) | 769 | 640 |
| 3Γ8         | 38.3770(309.531) meV (cm⁻¹) | 53.8 | 54 |
| 4Γ8         | 39.5973(319.374) meV (cm⁻¹) | 370 | 260 |
| 5Γ8         | 39.6789(320.032) meV (cm⁻¹) | 359 | 376 |
| 6Γ8         | 39.9118(321.910) meV (cm⁻¹) | 32.1 | 23 |
| 7Γ8         | 41.4748(334.517) meV (cm⁻¹) | 5.1 | 17 |
| 8Γ8         | 42.0494(339.151) meV (cm⁻¹) | 2.23 | 12 |
| 9Γ8         | 42.1602(340.045) meV (cm⁻¹) | 27.4 | 31 |
| 10Γ8        | 42.0494(339.151) meV (cm⁻¹) | 3.37 | 3 |
| 11Γ8        | 42.7180(344.544) meV (cm⁻¹) | 27.1 | 36 |
|             | 42.7540(344.834) meV (cm⁻¹) | 50.6 | 42 |
|             | 42.9361(346.303) meV (cm⁻¹) | 6.43 | 5 |
|             | 43.1677(348.171) meV (cm⁻¹) | 7.62 | 1.7 |
|             | 43.2853(348.982) meV (cm⁻¹) | 10.9 | 0.01 |
|             | 43.3505(349.28) meV (cm⁻¹) | 0.611 | 1 |
|             | 43.4799(350.689) meV (cm⁻¹) | 2.48 | 3.8 |

C. Lattice Absorption and Vibrational Modes

Dipole moments resulting from the lattice vibrations in Si are not first order and, hence, even though there are two Si in unite cell, Si cannot have single phonon absorption. In homopolar diamond-like structures, the absorption of the photon can be described by the simultaneous interaction of two phonons. The first phonon will induce a local charge distortion and the second phonon will simultaneously interact with this charge distortion and produce a temporary dipole moment. This dipole moment can then couple to the incident radiation. The two phonons are usually from two different crystallographic direction. In Si, the multiphonon absorptions are infrared active and they can readily be seen in the absorption spectra. Johnson (Ref. 45) has measured the optical absorption of Si and has assigned several absorption lines to the two- or three-phonon absorption.

It is important to note here that the oxygen (O) vibrational modes in Si are also infrared active. Oxygen which enters Si interstitially results in complex of SiO₂. The fundamental normal modes of vibration of this complex is explained to be the root of some infrared absorption. Several vibrational modes take place. The \( \nu_2 \) vibrational modes happen at 29.3, 37.8, 43.3 and 49.0 cm⁻¹ and the \( \nu_3 \) vibrational modes are a stem of 1136 cm⁻¹ vibration bands. Temperature-dependent effects arise when transitions occur from thermally populated of the excited states of the \( \nu_2 \) mode. This absorption happens at 1127.9 cm⁻¹.
Transmittance measurements were done by Bruker 113v FTIR spectrometer with Hg source and 4.2K Si bolometer detector pair for far infrared (400-5000 cm$^{-1}$) and Drude-Lorentz detector pair for mid infrared (10-100 cm$^{-1}$) ranges. Resolution at low temperatures (10-100 K) was 0.5 cm$^{-1}$ and at higher temperatures (100-300 K) was 4 cm$^{-1}$. The near-infrared spectra (4000-12000 cm$^{-1}$) were measured by using a Perkin Elmer 16U grating spectrometer. In this case, tungsten filament source and photoconductive detector (PbS) pair was used during measurements.

### III. ANALYSIS

#### A. Beer-Lambert Law

From the transmittance of a sample ($T = I_t/I_0$), assuming no reflection, we can extract the absorption coefficient from the Beer-Lambert law

$$T = \frac{I_t}{I_0} = e^{-\alpha t} \rightarrow \alpha = -\frac{1}{t} \ln \left( \frac{I_t}{I_0} \right), \quad (7)$$

where $t$ is the thickness of the sample and $\alpha$ is the absorption coefficient which is related to absorption cross section $\sigma_{abs}$ and the concentration of absorbing species $n_i$ through $\alpha = \sigma_{abs} n_i$.

Since the actual transmission is not that simple because there might be multiple reflection and transmission inside of the sample, more rigorous approach should be taken$^{5-8,31}$. The transmittance of a thick sample which causes the light to be incoherent is

$$T = \frac{(1 - R_{12})^2 e^{-\alpha x}}{1 - R_{12}^2 e^{-2\alpha x}}, \quad (8)$$

where $R_{12}$ is the reflectance at the front surface of the sample

$$R_{12} = \left| \frac{1 - \tilde{n}}{1 + \tilde{n}} \right|^2 = \frac{(n - 1)^2 + \kappa^2}{(n + 1)^2 + \kappa^2}. \quad (9)$$

The absorption coefficient is related to extinction coefficient through $\alpha = 2\omega\kappa/c$. If the absorption of a sample is small enough, that $\kappa \ll n$ then Equations 8 and 9 can be written as

$$e^{\alpha x} = \frac{(1 - R_{12})^2}{T} \left[ 1/2 + \sqrt{1/4 + \frac{R_{12}^2 - T^2}{1 - R_{12}^2}} \frac{R_{12}^2 T^2}{(1 - R_{12})^4} \right]$$

$$R_{12} = \left( \frac{n - 1}{n + 1} \right)^2. \quad (10)$$

Therefore, knowing the refractive index of the sample $n$, $\alpha$ could be extracted from these set of formulas.

Here we can define a more general quantity, integrated absorption or spectral weight $S$, which would be approximately independent of spectral resolution$^{23}$

$$S = \int_{\tilde{v}_{\min}}^{\tilde{v}_{\max}} \alpha(\tilde{v}) d\tilde{v} = K_S n_i, \quad (11)$$

where $K_S$ is an integrated absorption factor and the integration is over spectral extent of the isolated line. Here the wavenumber is denoted by $\tilde{v}$. The concentration of a given impurity would be then an integrated calibration factor (i.e., $K_S^{-1}$) multiplied by $S$.

#### B. Drude-Lorentz models

Using absorption coefficient ($\alpha$) and assuming constant refractive index $n$, the real part of the optical conductivity ($\sigma_1$) of the sample could be obtained through

| Sample ID | Type | Thickness/cm | Resistivity/$\Omega\cdot cm^{-1}$ | Concentration/$cm^{-3}$ |
|-----------|------|--------------|-------------------------------|--------------------------|
| si-jge    | n-type/Float zone | 1.29 | N/A | N/A |
| si-st1    | n-type/Czochralski | 2.02 | 0.17 | 3.9x10^{16} |
| si-st2    | n-type/Czochralski | 2.02 | 2.8 | 1.6x10^{15} |
| si-st4    | n-type/Float zone | 2.02 | 808 | 5.2x10^{12} |
| si-8547   | n-type/Czochralski | 0.63 | 134 | 3.18x10^{13} |
| si-8548   | p-type/Czochralski | 0.63 | 159 | 8.37x10^{13} |
| si-8549   | n-type/Float zone | 0.63 | 2950 | 1.39x10^{12} |
| si-8550   | p-type/Float zone | 0.63 | 115 | 1.16x10^{14} |
| si-8551   | n-type/Float zone | 0.63 | 10100 | 4.00x10^{11} |
| si-8552   | p-type/Float zone | 0.63 | 28500 | 4.67x10^{11} |

$a$ As determined from resistivity using the ASTM standard$^{10}$

$b$ Two samples of same type but taken from different parts of the boule

TABLE III. Samples measured
FIG. 1. Transmittance of samples measured from 20 or 40 cm$^{-1}$ to 11,000 cm$^{-1}$.

The transmittance values are plotted for different temperatures and frequencies. The transmittance values range from 0.0 to 1.0.

The transmittance values are shown for the following samples:
- si-jge
- si-st1
- si-st4
- si-st2
- si-8551
- si-8552

The frequencies range from 20 to 10000 cm$^{-1}$.

The relation in cgs units is given by:
\[
\alpha = \frac{2\omega \kappa}{c} = \frac{4\pi \sigma_1}{nc},
\]
where \(\kappa\) is the extinction coefficient. A Drude model was used to fit the free carrier part of the conductivity spectra. The equations for optical conductivity in the Drude part of the model are:
\[
\sigma = \frac{n_e e^2 \tau / m}{1 - i\omega \tau}
\]
\[
\sigma_1 = \frac{\sigma_{dc}}{1 + \omega^2 \tau^2}
\]
\[
\sigma_2 = \frac{\omega \tau \sigma_{dc}}{1 + \omega^2 \tau^2},
\]
where \(\tau\) is the scattering time, and \(\sigma_{dc}\) is the conductivity when \(\omega=0\). Here, it is interesting to look at the Drude conductivity \(\sigma_1(\omega)\). If we integrate the conductivity from
FIG. 2. Transmittance of samples from 20 or 30 cm$^{-1}$ to 4500 cm$^{-1}$.

$0$ to $\infty$ frequency we get

$$\int_{0}^{\infty} d\omega' \sigma_1(\omega') = \frac{1}{8} \omega_p^2 = \frac{\pi}{2} \frac{n_e e^2}{m}. \quad (14)$$

This equation is the sum rule for the Drude conductivity, and is independent of $\tau$. This equation says that an increase in the conductivity at low frequencies, for example, is offset by a decrease at higher frequencies. It should also be noted that the partial sum rules can be applied if the integral is carried out from $0$ to some frequency $\omega$. Then only the effective concentration of electrons participating in optical transitions at frequencies lower than $\omega$ would be involved. Eq. (14) changes to

$$\frac{\pi}{2} \frac{n_{e\text{eff}} e^2}{m^*} = \int_{0}^{\omega} d\omega' \sigma_1(\omega'). \quad (15)$$

This equation would be important in fitting for the free-carrier term in the conductivity spectrum.
IV. RESULTS AND DISCUSSION

A. Transmittance spectra

We have measured transmission spectra of various Si samples at different doping levels. Some of the samples were measured all the way to the band edge of Si. Others to about half of the bandgap.

FIG. 3. Optical conductivity $\sigma_1$ of sample si-jge. Lines are attributed to P.

FIG. 4. Optical conductivity $\sigma_1$ of sample si-st1. P-doped.

B. Transition lines

First, we discuss the sharp absorption lines that appear in the far infrared due to impurities in the n-type Si samples. Fig. 3 shows the far-infrared optical conductivity spectra of sample si-jge. The various transition lines were identified. They are due to the P impurity whose experimentally determined ionization energy is 45.578 meV. In samples with high impurity level, some of the transition lines had to be truncated because the transmittance is zero within the noise and accuracy of the measurements. For these lines, the absorption coefficient and thus the optical conductivity could not be calculated since when inverting Eq. 10, it results in taking natural logarithm of transmittance. Since the ln(1/T) is undefined, the integrated optical conductivity and the full width at half maximum of the lines are undefined too. Also, we observe that at the intermediate temperatures, there are absorption lines which are below the lowest transition energy of the ground state (i.e., $1S(A_1) \rightarrow 2P_0$). These lines are actually from the valley-orbit split ground states of $1S(E)$ and $1S(T_2)$ because they become thermally populated at the intermediate temperatures. Similar transition lines were observed for sample si-st4 (Fig. 6) and si-8551 (Fig. 7).

If we now look at si-st2 (Fig. 5), we can also observe the transitions from both ground state and valley-orbit split ground states to higher states of P impurity. But they are shifted towards the lower energies than for more pure samples. This shifts actually expected for double donor absorption (i.e., P donor pairs) in a Si sample due to heavier doping. For si-st1, at higher temperatures (100-300 K), we observe some transmission in the mid infrared range, yet we do not observe any transmission in the far infrared range. This opacity is because the sample has a high impurity concentration. Free-carrier...
FIG. 5. Optical conductivity $\sigma_1$ of sample si-st2. Sharp lines due to P.
absorption, coming from electrons ionized from the P atoms, dominates in the far infrared. As temperature decreased below 100 K, some transmission started to happen below 200 cm\(^{-1}\) and some absorption lines started to appear. These lines again correspond to P lines in Si, and, since the band of impurities become wide enough, we can no longer see any sharp transition lines corresponding to \(1S(A_1/E/T_2) \rightarrow nP_{\Omega/\pm}\) like transition. Instead, we observe a strong absorption edge. For the p-type Si, sharp absorption lines appear due to the B impurity in Si, whose experimentally determined ionization energy is 45.63 meV\(^{11}\). In Fig. 8 and 9, you can see the far infrared optical conductivity spectra of si-8548 and si-8550, respectively. The various transition lines were identified. They are due to ground state \(1\Gamma_8\) to excited state \(n\Gamma_8\) transitions in boron. These are so called \(p_{3/2}\) spectra that appear for acceptors in Si. A convolution of some B lines, which are close to each other in the spectrum, are observed due to the limitation in the instrumental resolution. There are no temperature dependent transitions appearing for this case because the spin-orbit-split ground state \(1\Gamma_7\), which lies in the band gap, remains depopulated up to room temperature\(^{22}\).

C. Oscillator strength of hydrogen-like states

The temperature dependence of the integrated optical conductivity of transition lines are given in Fig. 10.\(^{14}\) The behavior is as expected. Transition from the ground state to excited states become weak as temperature increases from the lowest temperature, as the ground state becomes depopulated with increasing temperature. Whereas for n-type Si, valley-orbit-split ground state to excited state transition is strong at intermediate temperatures. The integrated optical conductivity for many lines could not be calculated either due to transmission going being zero within the noise or not enough temperature points to see the behavior. For p-type Si, some of the B lines are in close proximity, so the integration is done through spectral extent of several lines which are indicated on the figures.

D. Multiphonon absorption

Multiphonon absorption happens in the midinfrared range for Si. As discussed in Sec. IIC the Si cannot have a single phonon absorption. The behavior of multiphonon absorption lines with temperature is as expected for all of the samples. The optical conductivity is shown.
FIG. 10. Integrated optical conductivity vs temperature for some of the lines in sample si-ige. P doped.

FIG. 11. Integrated optical conductivity vs temperature for some of the lines in sample si-st4. P doped.

FIG. 12. Integrated optical conductivity vs temperature for some of the lines in sample si-8551. P doped.

FIG. 13. Integrated optical conductivity vs temperature for some of the lines in sample si-8548. B doped.

FIG. 14. Integrated optical conductivity vs temperature for some of the lines in sample si-8550. B doped.

for two of the samples in Fig. 15 and 16 since they represent the behavior of multiphonons for all of the samples. The linewidth narrows as temperature is decreased since lattice vibrations relax. The strongest absorption at around 600 cm$^{-1}$ for some of the samples had to be cut of since the transmittance is zero within the noise and accuracy of the measurements.
FIG. 15. Multiphonon spectra for sample si-8552

FIG. 16. Multiphonon spectra for sample si-st2

FIG. 17. $\nu_2$ vibrational modes of Si$_2$O vibrations for sample si-st2

FIG. 18. $\nu_3$ vibrational modes of Si$_2$O vibrations for sample si-st4

FIG. 19. $\nu_3$ vibrational modes of Si$_2$O vibrations for sample si-8547

FIG. 20. $\nu_3$ vibrational modes of Si$_2$O vibrations for sample si-8548

FIG. 21. $\nu_3$ vibrational modes of Si$_2$O vibrations for sample si-8549

FIG. 22. $\nu_3$ vibrational modes of Si$_2$O vibrations for sample si-8550
FIG. 23. $\nu_3$ vibrational modes of Si$_2$O vibrations for sample si-8551

FIG. 24. $\nu_3$ vibrational modes of Si$_2$O vibrations for sample si-8552

FIG. 25. $\nu_3$ vibrational modes of Si$_2$O vibrations for sample si-8552*

E. Oxygen impurities

Absorption lines in the very far infrared due to the $\nu_2$ mode of vibration of the Si$_2$O complex, and modes due to the $\nu_3$ vibrational mode in the mid infrared were observed for some samples (see Sec. I C). The only absorption lines for sample si-8552 (p-type, highest purity) was observed in the mid infrared range. They are due to the $\nu_3$ vibrational modes (Fig. 24). For sample si-st2, in addition to $\nu_3$ vibrational mode in the mid infrared, the $\nu_2$ vibrational mode was observed at low temperatures (Fig. 17). For all other samples, except for si-jge and si-8551, the $\nu_3$ vibrational modes were observed in mid infrared ranges. Due to its high O content, the $\nu_3$ vibrational mode frequency of sample si-st1 has zero transmission to the extent of measurement accuracy. Also, temperature sensitive absorption at $\sim$1127.9 cm$^{-1}$ is seen for samples. This band is almost completely frozen out at the lowest temperatures where $\nu_3$ vibrational mode becomes intense. This behavior is attributed to thermal population of the excited states of the $\nu_2$ mode.

F. Unidentified absorption lines

Apart from these, we noticed some ambiguous transitions. For sample si-jge, we observe transitions which are similar to thermally populated $1S(E)/1S(T_2) \rightarrow nP_{0/\pm}$ like transitions at 66.8 meV and also $1S(A_1) \rightarrow nP_{0/\pm}$ like transition at 73.4 meV (Fig. 26). The latter was also observed for p-type samples si-8548 and si-8550. These lines had transition energy that were higher than those of typical shallow donors or acceptors transition and lower than deep-center transitions. However, they are close to shallow Cu acceptor transition in Si (65.8 and 68.7 meV) and also to $S_3X_3$ single donor transition in Si (70.45 and 75.769 meV). There is also transition line appearing at 202.7 cm$^{-1}$ (25.14 meV) for samples si-8551 and si-st4 (labeled as * in Figs. 6 and 7). If this transition is assumed to be of the $1S(A_1)/nP_{0/\pm}$ type due to it being highest in strength at the lowest temperature, and since the position for higher $2P_0$ or $2P_\pm$ states for donors is pretty well established, then the position of the ground state of this line should be either 36.63 or 31.54 meV which is close to the lithium (Li) ground state energy level in Si (31.24 meV for $1S(A_1)$ in Si:Li).

V. CONCENTRATION DETERMINATION

A. From the absorption lines $2P_0$, $2P_\pm$, $3P_0$ of P impurity and $1\Gamma_{8-}$, $2\Gamma_{8-}$ and $(3\Gamma_\pm \oplus 1\Gamma_\pm \oplus 4\Gamma_\pm)$ of B impurity

The observed linewidths, after accounting for instrumental broadening, are limited by several mechanisms.
and hence the maximum absorption coefficient $\alpha_{\text{max}}$ cannot be taken as a measure to determine the impurity concentration via Beer’s law. The absorption line has to be integrated through the spectral extent of the line, around the central frequency of absorption. This process ensures that the instrument’s limit on resolution does not affect the concentration determination. As stated in Sec. [IIIA], the integrated absorption $S$ is through Eq. [11] and concentration could be determined through

$$n_i = K_{S}^{-1} S$$

The absorption lines at $2P_0$ ($\sim 275$ cm$^{-1}$), $2P_\pm$ ($\sim 316$ cm$^{-1}$), $3P_0$ ($\sim 324$ cm$^{-1}$) were used to determine the P dopant concentration. The $1\Gamma^- \pm$ ($\sim 245$ cm$^{-1}$), $2\Gamma^- \pm$ ($\sim 278$ cm$^{-1}$) and $1\Gamma^- \mp 1\Gamma^- \mp 4\Gamma^- \pm$ ($\sim 320$ cm$^{-1}$) lines were used to determine boron dopant concentration. The latter is integrated through spectral extent of three lines because the lines are close together (see Tab. [II]) and cannot be resolved and integrated separately. The experimentally determined calibration factors are

$$K_{S}^{-1} = \begin{cases} 
4.2 \times 10^{13} \text{ cm}^{-1} & \text{for } 275 \text{ cm}^{-1} \\
1.2 \times 10^{13} \text{ cm}^{-1} & \text{for } 316 \text{ cm}^{-1} \\
23 \times 10^{13} \text{ cm}^{-1} & \text{for } 324 \text{ cm}^{-1} 
\end{cases}$$

of P,

$$K_{S}^{-1} = \begin{cases} 
6.8 \times 10^{13} \text{ cm}^{-1} & \text{for } 245 \text{ cm}^{-1} \\
1.5 \times 10^{13} \text{ cm}^{-1} & \text{for } 278 \text{ cm}^{-1} \\
1.7 \times 10^{13} \text{ cm}^{-1} & \text{for } 320 \text{ cm}^{-1} 
\end{cases}$$

of B,

where the latter is given for the 320 cm$^{-1}$ band which is the spectral extent of three lines. For some of the transition lines, $S$ could not be determined because the transmission was zero within the noise and accuracy of the measurements which made shape of the line and $\alpha_{\text{max}}$ incorrect. Also, the intensity of some of the lines was
too low and blended with noise of the background so no accurate $S$ was determined. The concentration of the impurities calculated through this method ($n_i(S)$) are given in Table IV.

### B. Concentration from oscillator strengths

Concentration of the samples were also determined from the oscillator strength calculated by Ref. 42 and 43 for P impurity in Si and by Ref. 44 and 45 for B impurity in Si. There, the $S$ of the lines was divided by corresponding theoretical oscillator strength at the lowest temperature achieved. Then the concentration was determined by

$$N = \frac{Q \times 10^{12}}{f_{th}} IA$$  \hfill (16)

(samples si-jge, si-st1, si-st2, si-8547, si-8548, and si-8550 show Drude like free carrier absorption in the far infrared range of frequencies. If we now consider the fact that the refractive index is relatively constant in this range, we can use sum rule for absorption (Eq. 15) to figure out the carrier concentration [57]. The fit to the optical conductivity was done by least square fits [50]. Fits to the optical conductivity are shown in Fig. 27 through Fig. 32. The insets show the behavior of Drude conductivity with temperature. From the Drude conductivity fit to the 300 K, we deduced the spectral weight which is $\omega_p$, central frequency ($\omega_0 = 0$ for Drude model), and a damping constant $\gamma = 1/\tau$. From the formula for the plasma frequency (Eq. 14), we determined the concentration for the samples above using corresponding conductivity effective masses (Sec. IB). Tab. 1 IV shows corresponding carrier concentrations ($n_i$ (Drude)) found from plasma frequency. The behavior of the carrier concentration and the damping constant are shown in Fig. 33 through Fig. 38. The carriers freeze out as the temperature is decreased, which means that donor or acceptor centers become neutralized. It is important to note here that sample si-8547 shows Drude carrier absorption, but using $Q = 0.987$ (Si:P) and $Q = 0.907$ (Si:B). Here, $f_{th}$ is the calculated values from Table I and Table II. The concentration was determined from various lines and then averaged. The average and standard deviation of $n_i$ are given in Table IV using this method ($n_i$ (OS)).

### C. Concentration from Drude absorption
TABLE IV. Concentration determined by several methods

| Sample ID/Type       | \( \rho \) (vendor) \( \Omega \text{ cm}^{-1} \) | \( n_i \) (vendor) \( \text{cm}^{-3} \) | \( n_i \) (S) \( \text{cm}^{-3} \) | \( n_i \) (OS) \( \text{cm}^{-3} \) | \( n_e \) (Drude) \( \text{cm}^{-3} \) |
|---------------------|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| si-jge/n-type       | N/A                             | N/A             | (8.5\pm1.3) \( \times 10^{13} \) | (5.6\pm1.3) \( \times 10^{13} \) | (5.2\pm0.2) \( \times 10^{13} \) |
| si-st1/n-type       | 0.17                            | 3.9\times10^{16} | -               | -               | (3.0\pm0.1) \( \times 10^{16} \) |
| si-st2/n-type       | 2.8                             | 1.6\times10^{15} | -               | -               | (1.7\pm0.1) \( \times 10^{15} \) |
| si-st4/n-type       | 808                             | 5.2\times10^{12} | (8.06\pm1.39) \( \times 10^{12} \) | (6.1\pm0.9) \( \times 10^{12} \) | -               |
| si-8547/n-type      | 134                             | 3.18\times10^{13} | -               | -               | (5.50\pm0.11) \( \times 10^{13} \) |
| si-8548/p-type      | 159                             | 8.37\times10^{13} | (8.07\pm0.55) \( \times 10^{13} \) | (6.63\pm0.91) \( \times 10^{13} \) | (8.45\pm0.14) \( \times 10^{13} \) |
| si-8549/n-type/     | 2950                            | 1.39\times10^{12} | (1.04\pm0.13) \( \times 10^{12} \) | -               | -               |
| si-8550/p-type      | 115                             | 1.16\times10^{14} | (1.34\pm0.05) \( \times 10^{14} \) | (1.06\pm0.13) \( \times 10^{14} \) | (1.06\pm0.01) \( \times 10^{14} \) |
| si-8551/[8551*]/n-type | 10100                          | 4.00\times10^{11} | [(1.18\pm0.10) \( \times 10^{12} \)]/[\] & [(8.0\pm0.6) \( \times 10^{12} \)]/[\] | -               |
| si-8552/[8552*]/p-type | 28500                          | 4.67\times10^{11} | -               | -               | -               |

FIG. 35. Carrier concentration and damping constant behavior with temperature for sample si-st2

FIG. 36. Carrier concentration and damping constant behavior with temperature for sample si-8547

FIG. 37. Carrier concentration and damping constant behavior with temperature for sample si-8548

FIG. 38. Carrier concentration and damping constant behavior with temperature for sample si-8550

does not show any sharp absorption lines at low temperatures except for \( v_3 \) vibrational mode of Si\(_2\)O. This could be attributed to the fact that oxygen in Si can become a thermal donor, which is an electrically active center, and contribute to free carrier absorption in far infrared spectra\(^{[58]}\).

VI. CONCLUSION

Most of our samples displayed a good optical transmission in infrared ranges which is a good sign for the immersion gratings. As we have previously noted, the high refractive index helps to reduce the instrument’s size or increase the resolution of a high resolution infrared spectrometers utilized in astronomy\(^{[60]}\). However, it is clear that the materials are much affected by the multiphonon absorption in the mid infrared and impurity absorption in far infrared. Therefore, these absorption ranges may not be helpful in identification and characterization of extrasolar planets. In addition, if Si has high oxygen content, the far infrared ranges of 10 - 30 cm\(^{-1}\) are not as feasible too due to \( v_2 \) vibrational mode of Si\(_2\)O.

Concentrations shown in Tab. [IV] are net impurity concentration and they do not account for compensated impurities. Samples si-8551*, si-8552 and si-8552* did not display any free carrier or impurity absorption so we could not determine the concentration. We attribute some discrepancy with the vendor concentration, which was determined from the vendor resistivity, to the fact that concentration obtained from transmission method is the average over the thickness of the samples, while the four-point probe method gives surface resistance which
is then converted to the bulk resistivity values. Also, the resistivity measurements require an Ohmic contact which is hard to achieve with highly resistive polished samples.

Overall, the transparency in the near infrared is pretty high and the Si is readily usable at that range of frequencies for astronomy. The samples displayed a good transmittance in the near infrared as long as the net impurity concentration was below $\sim 10^{15}$ cm$^{-3}$. So SIGs could be constructed and used in frequency range of $\sim 1500 - 8400$ cm$^{-1}$ ($\lambda \approx 1.2 - 6.6$ $\mu$m) at room temperature. At liquid helium temperature (namely $4.2$ K), due to band gap expansion, the high frequency limit can be extended to $\sim 9500$ cm$^{-1}$ ($\lambda \approx 1.05$ $\mu$m). It is obvious that for SIGs one needs to have as pure samples as possible but going below $\sim 10^{15}$ cm$^{-3}$ seems to be just enough for the near infrared regions.

For the midinfrared region, one is limited by the multiphonon absorption of the Si. Midinfrared multiphonon absorption appears in frequency range of $\sim 450 - 1500$ cm$^{-1}$ ($\lambda \approx 6.6 - 22.2$ $\mu$m), and it lessens a bit at low temperatures. However, it is still high and there is no good way of utilizing this region except when the multiphonon absorption is not as drastic.

In the far infrared, operating SIGs at room temperature will be limited by the far infrared multiphonon absorption that involves acoustical branch. However, it softens out as the temperature is decreased and SIGs could be utilized in the far infrared region which is in frequency range of $\sim 10 - 450$ cm$^{-1}$ ($\lambda \approx 22.2 - 1000$ $\mu$m). Yet, the Si has to be more pure than $\sim 10^{12}$ cm$^{-3}$ if to be utilized in these regions. This purity will ensure that the impurities will not affect the performance of SIGs. If not so pure samples are available, then at low temperatures, residual impurity absorptions dominate and some regions of far infrared are not feasible. One might want to avoid the $\nu_2$ vibrational mode of Si$_2$O, phosphorus and boron absorption lines to operate the instrument. For n-type samples, the useful range of frequencies would be $\leq 275$ cm$^{-1}$ ($\lambda \geq 36.4$ $\mu$m) which is the lowest transition of the P impurity in Si (i.e., $1S(\Gamma_8) \rightarrow 2P_0$ absorption line of Si:P). And also if it has too much oxygen content, then the range below $30 - 50$ cm$^{-1}$ is not usable because the $\nu_2$ vibrational modes of Si$_2$O happen in those regions. For the p-type samples, considering the boron impurity, the utilizing range would be $\leq 245$ cm$^{-1}$ ($\lambda \geq 40.8$ $\mu$m) due to the ground state to excited state transition (i.e., $1\Gamma_8^+ \rightarrow n\Gamma_n^-$ absorption line in Si:B). There might be some other impurities which might affect the far infrared transmittance of Si, but these usually are not as significant as P and B impurities in Si.

The behavior of impurities in Si is one that was expected for shallow impurities. At low temperatures we see hydrogenic like transitions and at intermediate temperatures we observe transitions from valley orbit split ground state. Concentrations were determined from $2P_0$, $2P_{3/2}$, $3P_0$ for n-type and $1\Gamma_8^-$, $2\Gamma_8^-$ and $(1\Gamma_6^+ \oplus 1\Gamma_7^- \oplus 4\Gamma_8^0)$ for p-type absorption lines, oscillator strengths at low temperatures and Drude absorption from room temperature. The nature of some of the lines were ambiguous and have yet to be understood at which stage of production they have appeared. Overall, the host material of SIGs need to be of high purity in order to give adequate performances which is going to be better (for transmittance will increase) for lower temperatures.

References:

1. J. Ge, B. Zhao, S. Powell, A. Fletcher, X. Wan, L. Chang, H. Jakeman, D. Koukis, D. B. Tanner, D. Ebbets, J. Weinberg, S. Lipsyc, R. Nyquist, and J. Bally, Proc. SPIE 8450, 84502U (2012).
2. J. P. Marsh, D. J. Mar, and D. T. Jaffe, Appl. Opt. 46, 3400 (2007).
3. H. Ohmori, N. Ebizuka, S. Morita, Y. Yamagata, and H. Kudo, Annals - Manufacturing Technology 50, 221 (2001).
4. G. Wiedemann and D. E. Jennings, Appl. Opt. 32, 1176 (1993).
5. S. Yim, H. Ohmori, Y. Uehara, T. Shimizu, and W. Lin, JSME International Journal Series C Mechanical Systems, Machine Elements and Manufacturing 47, 59 (2004).
6. J. Ge, B. Zhao, S. Powell, P. Jiang, B. Uzakbaiuly, and D. Tanner, SPIE 9143, Space Telescopes andInstrumentation 2014: Optical, Infrared, and Millimeter Wave, 91434T (2 August 2014).
7. S. Hild et al., Classical and Quantum Gravity 28, 094013 (2011).
8. G. Hammond, S. Hild, and M. Pitkin, Journal of Modern Optics 61, S10 (2014) pMID: 25705087, http://dx.doi.org/10.1080/09500340.2014.920934.
9. B. P. Abbott et al., Classical and Quantum Gravity 34, 044001 (2017).
10. K. Kuroda and the LCGT Collaboration, Classical and Quantum Gravity 23, S215 (2006).
11. J. Ge, B. Zhao, S. Powell, A. Fletcher, X. Wan, L. Chang, H. Jakeman, D. Koukis, D. B. Tanner, D. Ebbets, J. Weinberg, S. Lipsyc, R. Nyquist, and J. Bally, Proc. SPIE 8450, 84502U (2012).
12. J. P. Marsh, D. J. Mar, and D. T. Jaffe, Appl. Opt. 46, 3400 (2007).
13. J. Ge, B. Zhao, S. Powell, P. Jiang, B. Uzakbaiuly, and D. Tanner, SPIE 9143, Space Telescopes andInstrumentation 2014: Optical, Infrared, and Millimeter Wave, 91434T (2 August 2014).
14. S. Hild et al., Classical and Quantum Gravity 28, 094013 (2011).
15. G. Hammond, S. Hild, and M. Pitkin, Journal of Modern Optics 61, S10 (2014) pMID: 25705087, http://dx.doi.org/10.1080/09500340.2014.920934.
16. B. P. Abbott et al., Classical and Quantum Gravity 34, 044001 (2017).
