Light in strongly scattering semiconductors - diffuse transport and Anderson localization
Gomez Rivas, J.

Citation for published version (APA):
Gomez Rivas, J. (2002). Light in strongly scattering semiconductors - diffuse transport and Anderson localization
3 Near infrared transmission through powdered samples

Measurements of the total transmission in the near infrared through layers of randomly-packed Si and Ge micron-sized particles are presented in this chapter. In the wavelength range 1.4 – 2.5 μm, the scattering properties and the effect of residual absorption are analyzed. The sample-preparation method is explained in section 3.2. The measurements were done with a Fourier transform infrared spectrometer. The experimental set-up is described in section 3.3. Very strong scattering ($k\ell_s \approx 3$ at $\lambda_o = 2.5 \mu m$) and significant absorption at shorter wavelengths than 2 μm are measured in the Si samples [90, 94]. The energy density coherent potential approximation (EDCPA) is used to calculate the scattering mean free path and the localization parameter in the Si samples. We find good agreement between the calculations and the total-transmission experiments [85, 90]. In the Ge samples the total transmission decays exponentially with the sample thickness at all wavelengths in the studied range (section 3.5). This dependence of the total transmission can be due to strong localization or to optical absorption. By measuring the total transmission through the Ge samples filled with a non-absorbing liquid, a method which makes possible to discard or not optical absorption is introduced [91]. We find that in the Ge samples absorption has been introduced, presumably during the powder preparation.

3.1 Introduction

In spite of the great effort to localize light in systems formed by dielectric media [24, 75, 88, 120], there is no evidence of localization in such systems. Titanium dioxide TiO$_2$ is the dielectric with the highest refractive index in the visible $n = 2.7$ [130]. The lowest value of the localization parameter measured in TiO$_2$ samples is $k\ell_s \approx 7$ [24]. These samples were close-packed powders of particles with an average radius of 110 ± 35 nm. This average radius corresponds to the
maximum scattering cross section of Mie scatterers in the visible (section 1.1). Moreover, since the surrounding medium of the scatterers in a powder is air, the refractive index contrast in the TiO$_2$ powders is maximum.

Although probably a lower value of $k\ell_s$ can be reached in TiO$_2$ samples by reducing the polydispersity; most likely a refractive index contrast of 2.7 does not suffice to localize light. The scattering mean free path in TiO$_2$ samples will thus depend on the particle radius and wavelength as indicated by the upper line of Fig. 1.5, i.e., the localization transition is not reached in TiO$_2$ samples for any value of the scatterers radius and at any wavelength.

Some semiconductors, as it is shown in Fig. 1.6, have higher refractive indexes than TiO$_2$. They are good candidates for preparing materials where light is localized. The absorption coefficient of intrinsic semiconductors is very low ($\alpha \gtrsim 0.1\text{cm}^{-1}$) in a spectral window limited at short wavelengths by the semiconductor band gap $\lambda_{\text{gap}}$, and at long wavelengths by free-carrier absorption and phonon bands. Since it is believed that optical absorption destroys localization [42, 43], the search for localization is limited to this wavelength window.

Silicon is a thoroughly studied semiconductor. Its high refractive index $n = 3.5$ [132], its non-toxic properties, and the ease with which it can be obtained, persuaded us to start the localization experiments with Si powders. The band gap of Si is at $\lambda_{\text{gap}} = 1.1\ \mu m$, which limits the experiments to the infrared.

Germanium has an even larger refractive index than Si, $n = 4$ [133]. Therefore, we also decided to study the propagation of light in Ge powders. The band gap of Ge is at $\lambda_{\text{gap}} = 1.85\ \mu m$.

A few months after the work presented in this thesis was initiated, localization of near-infrared radiation $\lambda_0 = 1.067\ \mu m$ was reported in GaAs powders [76]. GaAs particles were made by milling intrinsic semiconductor. Total-transmission and enhanced-backscattering measurements were performed in three kind of GaAs samples with different average particle radius $r \approx 5, 0.5$ and $0.15\ \mu m$. The size of the particles was regulated by the time that the material was milled.

The measurements in the GaAs samples with $r \approx 5\ \mu m$ particles could be explained in terms of classical diffusion. The big particle size compared to the wavelength leads to a small scattering cross section and an inefficient scattering (section 1.1). In the samples with particles of average radius $r \approx 0.5\ \mu m$, the total transmission decreased with the inverse of the square of the sample thickness. According to Eq. (2.61), these samples are close to the localization transition. The EBS measurements on these samples could not be explained with classical diffusion theory. The exponential decay of the total transmission with the size of the samples with the smallest particles, and the rounding of the EBS cone of these samples were attributed to strong localization.
The interpretation of these measurements in terms of Anderson localization was questioned [77]. Since the milling time is longer for the samples with the smallest particles, Scheffold et al. [77] reasoned that in these samples stronger absorption introduced during the preparation might be expected. These authors claimed that the transmission and the EBS measurements could be then explained by classical diffusion with optical absorption.

This disagreement in the interpretation of the measurements in GaAs powders made clear that systematic studies of the optical scattering and absorption in semiconductor powders were necessary.

### 3.2 Sample preparation

The starting materials for the fabrication of the samples were commercially available Si and Ge powders.\(^1\) The Si powder was formed by polycrystalline particles with sizes ranging from a few hundred nanometers to about 40 μm and with a purity of 99.999%. The Ge powder had a purity larger than 99.999% and the particle size was smaller than 150 μm.

To reduce the polydispersity of the Si powder, the particles were suspended in spectroscopic-grade chloroform and they were let to sediment for 300 s. Only the particles that did not sediment were used in the experiments. The Ge powder was first milled at low speed.\(^2\) A zirconia beaker and balls were used for the milling. After 240 s, 5 ml of spectroscopic-grade methanol were added and the suspension was milled during 60 s. The resulting particles were sedimented during 150 s.

The particle size and polydispersity were evaluated from SEM photographs like the ones shown in Figs. 3.1 (a) and (b). Figure 3.1 (a) corresponds to Si particles, while in Fig. 3.1 (b) Ge particles are shown.

---

\(^1\) Si: Cerac S-1049; Ge: Aldrich 32739-5

\(^2\) The milling was done with a planetary micro mill, Pulverisette 7, Fritsch GmbH.
As can be seen in the figure, the Si particles tend to aggregate into clusters. This makes the definition of their radius difficult. The average radius of the particles was evaluated with two different methods: a) considering all the particles as entities, independently of whether or not they are part of a cluster, and b) considering the clusters as single particles. The radius of the particles (or clusters) was defined as half the Feret’s diameter, which is the distance between two tangents to the particle surface, parallel to some fixed direction, and on opposite sides of the particle [134]. Figure 3.2 shows the normalized histograms of the particle radius obtained with both methods. In general, particles prepared by milling or grinding present a log-normal distribution of sizes $y = C \exp[-\ln^2(r/r_c)/2W^2]$ [134]. The fit of this function to the histogram obtained with method a) gives $C = 0.90$, $r_c = 0.19 \mu m$, $W = 0.61$, and it is shown by the solid line in Fig. 3.2; while method b) gives $C = 0.86$, $r_c = 0.44 \mu m$, $W = 0.55$, and it is represented by the dashed line in the same figure. These fits allow to calculate the average radius of the particles and its standard deviation: a) $r = 0.33 \pm 0.22 \mu m$, and b) $r = 0.69 \pm 0.41 \mu m$. The polydispersity, defined as the ratio between the standard deviation and $r$ in percentage, is of 67% and 59% respectively. In other words, the Si samples are constituted of highly polydisperse scatterers.

For the Ge particles no aggregation was observed, making the determination of the particle radius simpler than in the case of the Si powders. From the fit of the histogram of the particle radius in the Ge powder with a log-normal distribution function the average radius was found to be $r = 2.1 \pm 0.9 \mu m$ and the polydispersity 43%.

To form layers of Si or Ge powders, a few drops of the suspensions were put on

![Figure 3.2:](image_url)

Normalized histograms of the radius of the silicon particles considering all the particles as entities, independently of whether or not they are part of a cluster (solid bars), and considering the clusters as single particles (dashed bars). The solid and dashed lines are log-normal fits, from which the average radius are calculated.
3.3. EXPERIMENTAL SET-UP

glass substrates and the chloroform or methanol was let to evaporate. The resulting samples are stiff slabs of close-packed Si or Ge particles in an air matrix.

The thickness \( L \) of the layers were measured by making scratches at the edges of the samples. With a calibrated microscope, with a resolution of \( 1 \mu m \), the images of the surface of the sample and the substrate were focused. The thickness is given by the difference between the focus points. For each sample the thickness was measured at different places within its central region to be sure that the layer was homogeneous. The thickness of the layer is defined as the average value of these measurements.

The volume fraction occupied by the particles, \( \phi \approx 40\% \), was determined by weighting the samples.

3.3 Experimental set-up

The set-up used for the total-transmission measurements is depicted in Fig. 3.3. The total transmission was measured with a Fourier transform infrared spectrometer (FTIR).\(^3\) The FTIR consists of a Michelson interferometer in which one mirror is fixed and the other is scanned over a distance of 8 cm at a velocity of 0.16 cm/s. The spectral resolution of the measurements was 8 cm\(^{-1}\). The signal produced on three detectors by the beam of a He:Ne laser (not plotted in Fig. 3.3) is used to calculate the displacement of the moving mirror and to perform the dynamic alignment. Small misalignments of the interferometer are automatically corrected by means of piezoelectric actuators on the fixed mirror.

The high stability of the FTIR allowed to perform several scans, which were averaged to increase the signal-to-noise ratio. Typically, between 250 and 1000 scans were averaged depending on the total transmission of the sample.

A tungsten-halogen lamp has been used as light source. Short wavelengths were optically filtered. A lens with a focal distance of 15 cm and an iris with a diameter of 2 mm, placed in front of the sample, insured that the total transmission was measured only in the region where the thickness was characterized.

The light transmitted diffusively was collected with a BaSO\(_4\) coated integrating sphere,\(^4\) and detected with a PbSe photoconductive cell. The total transmission is given by the Fourier transform of the interferogram. Before and after measuring each sample, the transmission through a clean glass substrate was recorded. This measurement was used as reference to obtain the absolute value of the total transmission through the samples and to check the stability of the set-up.

\(^3\)BioRad FTS-60A.

\(^4\)Labsphere ISO40SF
3.4 Total transmission through Si samples

Figure 3.4 shows a total-transmission spectrum of a sample of Si powder with a thickness of $L = 57.8 \pm 2 \, \mu m$ (solid line), and the transmission spectrum of a Si wafer (dashed line). For an easier comparison, both measurements have been normalized by their maximum transmissions. The sharp band gap ($\lambda_{\text{gap}} = 1.1 \, \mu m$) can be clearly observed in the spectrum of the Si wafer. The total transmission of the powdered sample is very low at wavelengths close to the band gap due to strong scattering and/or optical absorption. To quantify these two contributions, a series of samples with different thickness was measured. The total-transmission measurements of Si layers are plotted in Fig. 3.5 as a function of their thickness. The squares correspond to $\lambda_0 = 2.5 \, \mu m$ and the circles to $\lambda_0 = 1.4 \, \mu m$.

If the effective refractive index $n_e$ of the sample is known, the extrapolation lengths, $z_{e_1}$ and $z_{e_2}$, can be calculated using Eq. (2.17). The effective refractive index can be experimentally obtained from the measurement of the angular-resolved transmission (see section 2.2.3). This measurement is not easy to perform with a FTIR spectrometer due to the low intensity of the light source. As the volume fraction occupied by the particles is known to be $\approx 40\%$, $n_e$ can be estimated. Taking $n_e$ as the Maxwell-Garnett effective refractive index [116], we find $n_e \approx 1.5$ in the wavelength range $1.4 - 2.5 \, \mu m$. With this value of $n_e$, the extrapolation lengths of the Si-air and Si-substrate interfaces are $z_{e_1} = 2.42 \ell$ and $z_{e_2} = 0.78 \ell$ respectively. Note that reflections on the substrate-air interface will modify the value of $z_{e_2}$. If infinite reflections are considered $z_{e_2} = 2.4 \ell$ [135]. However, the value of $\ell$ obtained from the fits of Eq. (2.42) to the total-transmission measurements is independent of $z_{e_2}$ as long as $L \gg z_{e_2}$, which is the case in the investigated samples.

As it is shown by the solid lines of Fig. 3.5, the measurements of the total
3.4. TOTAL TRANSMISSION THROUGH SI SAMPLES

Figure 3.4:
Transmission spectra normalized to their maximum transmissions. Solid line: total-transmission spectrum of a layer of silicon powder with a thickness of 57.8 μm. Dashed line: transmission spectrum of a silicon wafer.

transmission can be fitted excellently by using classical diffusion theory. The fit of Eq. (2.42) to the $\lambda_o = 2.5 \, \mu m$ measurements yields $\ell = 0.83 \pm 0.08 \, \mu m$. At this wavelength $L_a \gg L$, thus absorption can be neglected. From the fit to the $\lambda_o = 1.4 \, \mu m$ measurements $\ell = 0.56 \pm 0.06 \, \mu m$ and $L_a = 8.8 \pm 1 \, \mu m$ are obtained.

The wavelength dependence of $L_a$ is plotted in Fig. 3.6. The increase of absorption for $\lambda_o < 2.0 \, \mu m$ is due to strain in the Si lattice structure. The presence of strain in the Si particles was confirmed from the width of X-ray diffraction peaks. Strain gives rise to a deformation of the potential, which smears the valence and conduction bands of the semiconductor. This deformation results in an edge of the band gap that extends into longer wavelengths than $\lambda_{\text{gap}}$. This absorption edge is known as the Urbach edge [136], and gives rise to an absorption length that

Figure 3.5:
Total transmission through Si powder versus the thickness of the sample $L$. The squares and the circles are the measurements at $\lambda_o = 2.5 \, \mu m$ and $\lambda_o = 1.4 \, \mu m$ respectively. The solid lines are fits using diffusion theory with $z_{e_1} = 2.42 \ell$ and $z_{e_2} = 0.78 \ell$. At $\lambda_o = 2.5 \, \mu m$ the transport mean free path is $\ell = 0.83 \, \mu m$, and optical absorption is negligible. At $\lambda_o = 1.4 \, \mu m$ the absorption length is $L_a = 8.8 \, \mu m$ and $\ell = 0.56 \, \mu m$. 
increases exponentially with the wavelength

\[ L_a \propto \exp \left( \frac{\lambda_0}{\lambda_U} \right). \]  

(3.1)

The fit of the measurements to Eq. (3.1) is represented by the line in Fig. 3.6, where \( \lambda_U = 0.15 \pm 0.01 \mu m \).

The transport mean free path \( \ell \) is plotted in Fig. 3.7 as a function of \( \lambda_0 \). C.M. Soukoulis from Iowa State University and K. Busch from the University of Karlsruhe have used the energy density coherent potential approximation EDCPA (see appendix A) to calculate the scattering mean free path in a random medium composed of Si spheres (\( \phi = 40\% \)) with a size distribution given by a log-normal function (\( C = 0.86, r_c = 0.44 \mu m, W = 0.55 \)). The solid line in Fig. 3.7 is a convolution of the calculated \( \ell_s \) for the specific sizes of the spheres with the probability density function given above.

As can be seen in Fig. 3.7, there is a good qualitative agreement between the measured \( \ell \) and the calculated \( \ell_s \). The quantitative difference can be attributed to several factors: first, with the EDCPA \( \ell_s \) is obtained, whereas the total-transmission measurements give \( \ell \). Second, for the EDCPA calculation the scatterers are considered perfect spheres, which clearly is not the case in the Si samples. Finally, as pointed out before, there is not an unambiguous way of measuring the particle radius due to the aggregation of Si particles. The best agreement between theory and experiments is found when the particle clusters are considered as single scatterers.

For comparison, in Fig. 3.7 we have also plotted the calculated \( \ell_s \) in a system composed by monodisperse Si spheres of radius 0.44 \( \mu m \) and a volume fraction of

![Figure 3.6: Absorption length in silicon powders versus the wavelength. The solid line is a fit to Eq. (3.1), with \( \lambda_U = 0.15 \mu m \).](image-url)
40% (dashed line). As can be seen in Fig. 3.7, the scattering mean free path in a polydisperse system is in general larger than in a monodisperse one. It is more favorable to have a medium formed by scatterers with the largest possible $\sigma_s$. A polydisperse sample will contain particles which efficiently scatter light, together with inefficient scatterers. Therefore, the high polydispersity in the particle size constitutes the main limitation to the scattering strength in the Si samples.

With the transport mean free path obtained from the measurements of the total transmission, and assuming that the Si particles are isotropic scatterers $\ell = \ell_s$,\(^5\) we can estimate the localization parameter, $k\ell_s = 2\pi n_e \ell_s / \lambda_o$. The values of $k\ell_s$ are plotted in Fig. 3.8 as a function of $\lambda_o$. The weak dependence of $\ell$ with $\lambda_o$, due to the high polydispersity in the samples, gives rise to a nearly constant scattering strength. The solid line in Fig. 3.8 represents the localization parameter using the values of $\ell_s$ that are obtained from the EDCPA calculation.

It must be stressed that, although the presented results can be explained using classical diffusion theory, the Si samples are very close to the critical value of $k\ell_s \approx 1$. In fact, the localization parameter $k\ell_s \approx 3$ at $\lambda_o = 2.5 \mu m$ is more than a factor of two smaller than the lowest value of $k\ell_s$ reported in TiO$_2$ powders [24].

3.5 Total transmission through Ge samples

The total-transmission spectrum of a sample of Ge powder with a thickness of $L = 12.4 \pm 1.2 \mu m$ is plotted in Fig. 3.5 (solid line). The band gap of intrinsic Ge

\(^5\)Note that by setting $\ell$ equal to $\ell_s$ interference effects are obviated.
is indicated in the same figure with an arrow.

Like with Si, the total transmission through Ge powder was measured in layers with different thickness. Figure 3.10 shows the total transmission versus the sample thickness at $\lambda = 1.7 \, \mu m$ (circles) and at $\lambda = 2.5 \, \mu m$ (squares). In the entire spectral range of the measurements the total transmission decreases exponentially with the sample thickness. The characteristic length of this exponential decay, named $L_d$, is plotted in the inset of Fig. 3.10 as a function of the wavelength. At $\lambda = 1.7 \, \mu m$ it is not surprising this dependence since $1.7 \, \mu m < \lambda_{gap}$, and strong absorption takes place.

**Figure 3.8:**
Localization parameter $k\ell_s$ in silicon powders versus the wavelength. The solid line is the localization parameter calculated with the EDCPA in a polydisperse system of Si spheres.

**Figure 3.9:**
The solid line is the total-transmission spectrum of a layer of Ge powder with a thickness of $L = 12.4 \, \mu m$. The open circles are the total-transmission spectrum of the same sample with the air voids filled with CCl$_4$. The arrow indicates the band gap of intrinsic Ge.
The interpretation of the total-transmission measurements at $\lambda_o > \lambda_{\text{gap}}$ is more complicated. The absorption coefficient of intrinsic Ge at sub-band gap wavelengths is very low [133]. The exponential decay of the total transmission as a function of the sample thickness at these wavelengths could be attributed to strong localization in a non-absorbing medium. It is also possible that during the sample preparation impurities have been added to the Ge powder or defects are created at the surface of the particles, giving rise to an increase of the absorption coefficient.

To determine which of these two situations (localization or absorption) applies, the total transmission of the samples filled with carbon tetrachloride CCl$_4$ was measured. In the wavelength range under investigation, CCl$_4$ has a refractive index of $n = 1.4$ and it does not absorb [137]. By filling the samples the refractive index contrast between the scatterers and the surrounding medium is changed from 4.1 to 2.9. Therefore, the scattering cross section is reduced or equivalently the scattering and transport mean free paths are increased.

The total-transmission measurement of the sample with a thickness of $L = 12.4 \, \mu m$ filled with CCl$_4$ is plotted in Fig. 3.5 (open circles). The higher transmission of the filled sample clearly confirms the increase of $\ell$. After letting evaporate the CCl$_4$, the original spectrum was recovered. This means that the structure of the samples did not change and that CCl$_4$ only filled the voids between Ge particles.

The complete infiltration of the samples was carefully checked by measuring the change of the specular reflection of a beam from a He:Ne laser on the bottom of the samples upon the addition of CCl$_4$.

A refractive index contrast of 2.9 should be too low to induce localization, moreover in a system that is highly polydisperse. As the optical absorption of CCl$_4$ is negligible, if the exponentially-decaying total transmission at $\lambda_o > \lambda_{\text{gap}}$...
is due to localization in a non-absorbing medium, the reduction of the refractive
index contrast should give rise to a total transmission described by the diffusion
approximation without absorption. On the other hand, if Ge absorbs significantly
at these wavelengths, the filled samples should have a finite absorption length, $L'_{a}$.
For clarity, the parameters of the filled samples will be denoted with a prime.

Figure 3.11 shows the total-transmission measurements at $\lambda_0 = 2.5 \mu m$ of the
Ge samples filled with CCl$_4$ as a function of the sample thickness. In the same
figure a fit to the measurements using classical diffusion theory is plotted with
a solid line. For the fit the extrapolation lengths are fixed to $z'_{e1} = z'_{e2} = (2/3)\ell'$
and the transport mean free path and absorption length are $\ell' = 1.53 \pm 0.1 \mu m$ and
$L'_a = 26 \pm 4 \mu m$. For comparison, the total transmission through a non-absorbing
medium with $\ell' = 1.53 \mu m$ is also plotted in Fig. 3.11 (dashed line).

As it has been mentioned in the preceding section, the value of $z'_{e2}$ does not
affect the analysis of the total-transmission measurements. On the other hand,
$\tau'_{e1} = z'_{e1}/\ell'$ needs to be carefully estimated to obtain a reliable value of $\ell'$. Carbon
tetrachloride forms a layer on top of the sample and $\tau'_{e1}$ depends on the reflections
on the Ge-CCl$_4$ and the CCl$_4$-air interfaces. To estimate $\tau'_{e1}$ the number of reflections
on these interfaces before the light leaks through the sample edges needs to
be known. The number of reflections will depend on the exact thickness of the
CCl$_4$ top layer [135], which is unknown. Therefore, in this experiment it is not at-
ttempted to obtain an accurate value of the transport mean free path, and by setting
$z'_{e1}$ to its value in the case of refractive index matched interfaces, i.e., $(2/3)\ell'$, the
transport mean free path is overestimated.

It is important to note that as $L'_a$ is obtained from the decay of the transmission
through the thickest samples, it is independent of the extrapolation lengths. As $L'_a$

Figure 3.11:
Total-transmission measurements of Ge samples filled with
CCl$_4$ as a function of the sample thickness. The solid line is
a fit using classical diffusion theory with $z'_{e1} = z'_{e2} = (2/3)\ell'$,
from which the absorption length $L'_a = 26 \pm 4 \mu m$ is
found. The dashed line is the expected total transmission in
a non-absorbing system with equal scattering strength.
for the filled Ge is of the order of $L$, we may conclude that the exponential decay of the total transmission in the non-filled Ge samples is not due to strong localization in a non-absorbing medium, but the role of absorption must be considered.

3.6 Discussion

As we have seen in section 3.4, in spite of the fact that the total-transmission measurements on Si powders can be fully described using diffusion theory, the localization parameter $k\ell_s \simeq 3$ at $\lambda_0 = 2.5 \mu m$ is more than a factor of two smaller than the lowest value of $k\ell_s$ found in TiO$_2$ powders [24]. These results confirm that semiconductor materials are good candidates to prepare a medium where light is localized.

A problem in the search for localization in Si and Ge powders arises from the significant optical absorption that they exhibit. Improvements in the reduction of the absorption can be achieved by annealing the particles to minimize the contribution of surface defects.

A remaining open question is why strong localization of near-infrared light is apparent in GaAs powders [76], while it is absent in similar samples of Si powders. According to the EDCPA [85, 86], for a given refractive index contrast, the localization parameter is much lower in the inverse structure than in the direct structure (see appendix A). The inverse structure is formed by air scatterers in a high dielectric material. A possible explanation for a lower value of $k\ell_s$ in the GaAs samples could be a different connectivity of the particles. If the contact between neighboring particles is better in the GaAs than in the Si samples, due to a different particle shape, the GaAs samples may be represented by an inverse structure. For the Si samples a description in terms of a direct structure could be more appropriate.

It is also possible that the results of Ref. [76] have been misinterpreted in terms of localization without optical absorption [77]. More experimental work must be done in the GaAs samples. A feasible experiment, as it is clearly shown in section 3.5, consists in filling the air voids in the GaAs samples with a non-absorbing liquid and measure the total transmission or the enhanced-backscattered intensity [79]. This experiment could confirm that the deviation from diffusion theory in the measurements of Ref. [76] are due to localization or if absorption is present in the GaAs samples.