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Ke Cao
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The Effect of Hydrogen on the Optical, Structural Properties and the Crystallization of GeTe₂ Thin Films Prepared by RF Magnetron Sputtering

by

Ke Cao

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science Department of Physics College of Art and Science University of South Florida

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Keywords: chalcogenides, amorphous, optical band gap, absorption coefficient, annealing, X-ray diffraction, Raman spectroscopy

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Dedicated to my parents
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Ke Cao

ABSTRACT

Thin films of GeTe₂ were deposited on glass substrates using RF magnetron sputtering with various hydrogen flow rates in the growth chamber. Transmission data of deposited films were taken and used to determine optical constants (refractive index (n), extinction coefficient (κ), and absorption coefficient (α)) and the energies: $E_{04}$, $E_{03}$, Tauc band gap $E_{\text{Tauc}}$ and Urbach energy $E_U$. An increase of these energies was observed with increasing hydrogen flow rate. This increase is interpreted on the basis of the density of state model proposed by Mott and Davis.

An increase of network disorder due to the inclusion of hydrogen into the GeTe₂ thin films was determined from the $B^{1/2}$ parameter, Urbach energy and full width at half maximum of Raman vibrational modes.

The crystallization process induced by thermal annealing on GeTe₂ was studied. X-ray diffraction measurements were performed and the results suggest that crystallization of GeTe₂ occurs via a phase separation into Te and GeTe crystalline phases. This observation is in agreement with a previous report. The crystallization temperature increases with the addition of hydrogen. This increase is explained in terms of dangling bonds. A large change (approximately 60% decrease) of the optical transmission occurs after the phase change from amorphous to crystalline. This decrease is interpreted as a result of the observed phase separation.
Chapter 1
Introduction

1.1 Overview of Chalcogenides Materials

Chalcogenide glasses are vitreous oxygen-free inorganic materials containing one or more of the chalcogen elements (Group VI): sulfur (S), selenium (Se), or tellurium (Te), but not oxygen (O), in conjunction with more electropositive elements such as zinc (Zn), Cadmium (Cd), silicon (Si), germanium (Ge), tin (Sn), phosphorus (P), arsenic (As), and antimony (Sb). They can be produced with widely varying stoichiometry in binary $A_xB_{1-x}$ and more complex compounds.

The amorphous chalcogenide semiconductors were discovered by in the 1950s by Kolomiets and Goryunova who discovered the first semiconducting glass $\text{TlAsSe}_2$. This was the first class of disordered semiconductors to be found. Later, in 1968, S.R. Ovshinsky and his co-workers from Energy Conversion Devices (Troy, Michigan, USA), discovered the memory and switching effects exhibited by some chalcogenide glasses. The unusual electrical effects in chalcogenides stimulated the development of the theory and applications of chalcogenide materials. From that time, new phenomena, properties and effects have been discovered in the non-crystalline chalcogenides. In parallel, the chalcogenides have truly emerged as multipurpose materials and have been applied in xerography, IR detection, holography, computer memories, radiometry and optical transmission of information. In recent years, thin films of amorphous chalcogenide glasses have been studied as phase change materials.

1.2 Phase Change Materials

The key properties that identify phase change materials feature the rapid and reversible transition between crystalline and amorphous forms in a nanosecond timescale as well as a pronounced difference of optical or electrical properties between amorphous...
and crystalline states. This optical contrast is evidence for a significant difference in the electronic states, which is not observed for conventional semiconductors such as GaAs, Si or Ge.\textsuperscript{2} The changes in the optical and electronic properties that accompany the transition provide ready means to monitor it. One unique behavior of some chalcogenides is that they can be "switched" back and forth between two states, crystalline and amorphous, with the application of heat. The crystalline and amorphous states of chalcogenide glass have dramatically different electrical resistivity and optical reflectivity, which forms the basis by which data is stored. This storage concept is sketched and explained in Fig. 1. In the amorphous phase, the material is highly disordered -- there is an absence of regular order to the crystalline lattice. In this phase, the material demonstrates high resistivity and low reflectivity. In contrast, in the crystalline phase, the material has a regular crystalline structure and exhibits high reflectivity and low resistivity. The amorphous, low reflectivity state is used to represent a binary 0, and the crystalline, high reflectivity state represents a 1.

Figure 1. Schematics of amorphous and crystalline states of phase change materials.\textsuperscript{3}

While this storage concept was proposed earlier in 1968 by Ovshinsky\textsuperscript{4}, interest in this class of materials has been rejuvenated in recent years.\textsuperscript{5-8} This is partly due to an increase in our knowledge of phase change materials.\textsuperscript{9,10} Since these alloys have been successfully employed in rewritable optical data storage the materials and their unique
properties are better understood\textsuperscript{11,12} than their predecessors in the late 1960s and early 1970s.

Phase change materials are widely used in optical storage media (CD-RW, DVD-RW, DVD-RAM and Blu-ray Disc) and have also become of interest for developing non-volatile electronic memory, the Phase Change Memory (PCM) device. PCM is positioned as a replacement for flash memory because it has non-volatile characteristics (that is, it is able to retain information even when all power to it is removed) and it is faster and can be scaled to smaller dimensions. Flash memory cells can degrade and become unreliable after as few as 10,000 writes, but PCM is much more resilient at more than 100 million write cycles. The next step in information technology is mobile computing and storage where any kind of information is potentially available everywhere for everyone. This requires devices that enable non-volatile memories.

The most common phase change materials are tellurium-based alloys, with the Ge\textsubscript{x}Sb\textsubscript{y}Te\textsubscript{1−x−y} family providing prototypes. Ge\textsubscript{x}Te\textsubscript{1−x} alloys were the first to show real promise as phase change storage media, and the widely studied Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} (GST) is used commercially in DVD-RAM (random access memory). The choice of GST was determined by its fast and stable performance and large reflectivity changes between the crystalline and amorphous states\textsuperscript{13}. Suitable materials for rewriteable optical storage that have been identified in the past few decades are shown in the schematic phase diagram of Fig. 2.

![Figure 2. Ternary phase diagram depicting different phase-change alloys.\textsuperscript{1}](image)
GeTe$_2$ has attracted interest in recent years due to the fact that GeTe$_2$ is the constituent of GeSbTe alloys. As shown in the phase diagram of GeSbTe alloys (Fig. 3), there are two pseudobinary lines passing through Ge$_2$Sb$_2$Te$_5$. They are GeTe$_2$–Sb$_2$Te and GeTe–Sb$_2$Te$_3$. Therefore, it is important to study the optical properties of these constituent materials in order to better understand the properties of GST.

![Figure 3. Phase diagram of the system Ge-Sb-Te.](image)

1.3 Hydrogen Incorporation

Hydrogen incorporation into amorphous Si (a-Si) has been found to improve the material properties. For example, amorphous silicon contains defects due to the presence of dangling bonds. Incorporated hydrogen atoms can bond with the dangling bonds and reduce the dangling bond density by several orders of magnitude. Therefore, hydrogenated amorphous silicon (a-Si:H) has a sufficiently low amount of defects to be used in devices. The realization of the doping of hydrogenated a-Si (a-Si:H) was a breakthrough that opened up many new areas for technological applications. Hence, it is of great interest to investigate the effect of hydrogen on other amorphous materials, for example IV-VI chalcogenides semiconductors.
1.4 Objective of This Work

In this thesis work, we studied the effects of H$_2$ on the refractive index, extinction coefficient, absorption coefficient, and optical band gap of GeTe$_2$ thin films. We also investigated the disorder of amorphous hydrogenated GeTe$_2$ films by examining the Urbach energy, Tauc parameter $B^{1/2}$ and Raman full width at half maximum (FWHM).

The other aim of this work is to investigate the crystallization of amorphous GeTe$_2$ thin films under thermal annealing and to study how the addition of hydrogen modifies the crystallization process. The change in optical properties of GeTe$_2$ thin films after amorphous-crystalline transformation is also studied.
Chapter 2
Optical Properties

2.1 Introduction

The study of optical properties of chalcogenides is very important for the
determination of electronic band structure as well as optical parameters, such as optical
energy gap, absorption coefficient, refractive index and extinction coefficient. Optical
properties are directly related to atomic structure, electronic band structure and electrical
properties, and hence are very important in device applications.

For crystalline semiconductors, the associated optical absorption spectrum
terminates abruptly at the fundamental gap, while in amorphous semiconductors a tail in
the absorption spectrum encroaches into the gap region\textsuperscript{15,16}. This tail in the optical
absorption spectrum, arising as a consequence of the tail and gap states, makes the optical
gap of an amorphous semiconductor difficult to be defined experimentally.

2.2 Derivation of Absorption Coefficient

In order to derive the absorption coefficient, we will use a semi-classical approach
to derive the Hamiltonian describing the interaction between an external electromagnetic
field and Bloch electrons inside a semiconductor. In this approach the electromagnetic
field is treated classically while the electrons are described by quantum mechanical
(Bloch) waves. We start with the unperturbed one-electron Hamiltonian:

\[ \hat{H}_0 = \frac{p^2}{2m_e} + V(r). \] (2.1)

We obtain the quantum mechanical Hamiltonian describing the motion of a charge \(-e\) in
an external electromagnetic field by replacing the electron momentum operator \(p\) by
\(p + (eA/c)\):

\[ \hat{H} = \frac{1}{2m_e} [p + (eA/c)]^2 + V(r), \] (2.2)
where $A$ is the vector potential of the electromagnetic radiation, $p$ momentum operator of electron. The term $\frac{1}{2m_e} [p + (eA/c)^2]$ can be expanded as
\[
\frac{1}{2m_e} [p + (eA/c)^2] = \frac{p}{2m_e} + \frac{e}{2m_e c} A \cdot p + \frac{e^2 A^2}{2m_e c^2}.
\] (2.3)

Using the definition of $p$ as the operator $\frac{\hbar}{i}\nabla$ we can express the term $\frac{eA}{m_e c} A \cdot p$ as
\[
(p \cdot A) f(r) = A \cdot \left( \frac{\hbar}{i} \nabla f \right) + \left( \frac{\hbar}{i} \nabla \cdot A \right) f.
\] (2.4)

Using the coulomb gauge $\nabla \cdot A = 0$, hence $(e/2mc)p \cdot A = (e/2m_e c)A \cdot p$. For the purpose of calculating linear optical properties we can also neglect the term $\frac{e^2 A^2}{2m_e c^2}$, which depends quadratically on the field. Under this assumption we can approximate $\hat{H}$ by
\[
\hat{H} = \hat{H}_0 + \frac{e}{m_e c} A \cdot p.
\] (2.5)

Compared with the unperturbed Hamiltonian $\hat{H}_0$, the extra term $\frac{e}{m_e c} A \cdot p$ gives the electron-photon interaction Hamiltonian $\hat{H}_I$.
\[
\hat{H}_I = \frac{e}{m_e c} A \cdot p.
\] (2.6)

We will now calculate the transition probability per unit volume $R$ for an electron in the valence band state $|v\rangle$ (with energy $E_v$ and wavevector $k_v$) to the conduction band $|c\rangle$ (with corresponding energy $E_c$ and wavevector $k_c$). To do this we need to evaluate the matrix element $|\langle c | \hat{H}_I | v \rangle|^2$:
\[
|\langle c | \hat{H}_I | v \rangle|^2 = (e/m_e c)^2 |\langle c | A \cdot p | v \rangle|^2.
\] (2.7)

The vector potential can be expressed as
\[
A = A \hat{e},
\] (2.8)

where $\hat{e}$ is the unit vector in the direction of the vector potential.

The amplitude of $A$ can be written as
\[
A = - \frac{E}{2q} \{ \exp[i(q \cdot r - \omega t)] + c. c. \}.
\] (2.9)

where $E$ and $q$ are electric field strength and wavevector of the electromagnetic radiation (photons), respectively, and c.c. stands for complex conjugate. Expanding $\exp[i(q \cdot r)]$ in series, as the photon wavevector is usually very small neglecting all terms dependent on $q$, one can write Eq. (2.9) as
\[ A \approx -\frac{E}{2q} [\exp(-i\omega t) + c.c.] \tag{2.10} \]

Using Eqs. (2.8) and (2.10) and note that \(cq = \omega\), one can rewrite Eq. (2.7) into

\[ |\langle c|\hat{H}_I|\nu \rangle|^2 = \left(\frac{eE}{2m_c \omega} \right)^2 |\langle c|\hat{\mathbf{e}} \cdot \mathbf{p}|\nu \rangle|^2. \tag{2.11} \]

In most cases, the matrix element \(\langle c|\hat{\mathbf{e}} \cdot \mathbf{p}|\nu \rangle\) is assumed to be independent of energy and wavevectors \(\mathbf{k}_c\) and \(\mathbf{k}_\nu\), and is written as

\[ \langle c|\hat{\mathbf{e}} \cdot \mathbf{p}|\nu \rangle = p_{cv}\delta_{k_c,k_v}. \tag{2.12} \]

### 2.2.1 Crystalline Solids

The case of c-solids will be presented first for comparison, because this theory is very well established. Applying the Fermi golden rule, the rate of absorption of photons per unit volume, due to transitions from valence to conduction bands, can be written as

\[ R = \frac{2\pi}{\hbar \nu} \sum_{k_c,k_v} |\langle c|\hat{H}_I|\nu \rangle|^2 \delta(E_c(\mathbf{k}_c) - E_v(\mathbf{k}_\nu) - \hbar \omega) \tag{2.13} \]

Substituting Eqs. (2.11) and (2.12) into Eq. (2.13) gives

\[ R = \frac{2\pi}{\hbar \nu} \left(\frac{e}{m_c \omega} \right)^2 \left(\frac{E(\omega)}{2} \right)^2 |p_{cv}|^2 \sum_{k_c,k_v} \delta(E_c(\mathbf{k}_c) - E_v(\mathbf{k}_\nu) - \hbar \omega) \delta_{k_c,k_v} \tag{2.14} \]

The rate of power loss per unit is given by

\[ W = R\hbar \omega \tag{2.15} \]

which can also be calculated from the rate of loss of incident energy per unit volume as

\[ W = -\frac{dl}{dt} = \frac{dl}{dx} \frac{dx}{dt} \tag{2.16} \]

Using \(I = I_0 \exp(-\alpha x)\), where \(\alpha\) is the absorption coefficient and \(x\) thickness of sample absorbing the light, one obtains from Eq. (2.16):

\[ W = \frac{\alpha cl}{n^2}. \tag{2.17} \]

where \(n\) is the refractive index of the material.

The energy density \(I\) can be related to the field amplitude by

\[ I = \frac{n^2}{8\pi} |E(\omega)|^2 \tag{2.18} \]

Comparing Eq. (2.15) with Eq. (2.17), we obtain

\[ \alpha = \frac{1}{nc} \left(\frac{2\pi e}{m_e^*} \right)^2 \left(\frac{1}{\nu \omega} \right) |p_{cv}|^2 \sum_{k_c,k_v} \delta(E_c(\mathbf{k}_c) - E_v(\mathbf{k}_\nu) - \hbar \omega) \delta_{k_c,k_v} \tag{2.19} \]
Note that the application of momentum conservation in Eq. (2.19) corresponds to a direct transition and it reduces the double summation (over $k_c$ and $k_v$) into a single summation ($k_c$ or $k_v$). Replacing the summation by an integration over the energy variable using

$$
\Sigma_k = \Sigma_E = \int g(E) dE ,
$$

where $g(E)$ is the DOS, one can write Eq. (2.19) as

$$
\alpha = \frac{1}{nc} \left( \frac{2\pi e^2}{m^*} \right)^{3/2} \left( \frac{1}{\nu_\omega} \right) |p_{cv}|^2 \int_{E_g}^{E_{cv}} g_j(E_{cv}) \delta(E_{cv} - \hbar\omega) dE_{cv}
$$

It should be noted that in Eq. (2.21), $g_j(E_{cv})$ is the joint DOS used for direct transitions in c-solids and it is calculated from the energy of both states, $E_{cv} = E_c(k) - E_v(k)$, $E_v(k)$ of the valence band (from which the electron is excited by creating a hole) and $E_c(k)$ of the conduction band (to which the electron is excited).

In bulk materials, the joint DOS can be expressed as

$$
g_j(E) = \begin{cases} 
\frac{\nu}{2\pi^2} \left( \frac{2\mu}{\hbar^2} \right)^{3/2} (E_{cv} - E_g)^{1/2} & E_{cv} \geq E_g , \\
0 & E_{cv} < E_g
\end{cases}
$$

where $E_g = E_c(0) - E_v(0)$, and $\mu$ is the reduced effective mass. From Eq. (2.22), it follows that the lower limit of integration in Eq. (2.21) is $E_g$, not zero. For solids, where this is not true (i.e. DOS below $E_g$ is non-zero), like in a-solids, the concept of joint DOS cannot be used. Substituting Eq. (2.22) into Eq. (2.21) gives

$$
\alpha = \frac{2}{nc^2} \left( \frac{e}{m^*_e} \right)^{3/2} \left( \frac{2\mu}{\hbar^2} \right)^{3/2} |p_{cv}|^2 (\hbar\omega - E_g)^{1/2} .
$$

Equation (2.23) demonstrates that plotting $(\alpha \hbar \omega)^2$ as a function of the photon energy $\hbar \omega$ gives a straight line that intersects the energy axis at $\hbar \omega = E_g$ and thus produces a sharp band edge for direct transitions in c-solids. The derivation of the absorption coefficient in a-solids will be presented in the next subsection.

### 2.2.2 Amorphous Solids

For a-solids, one should consider the transitions in different energy ranges separately. Let us first consider those transitions in which electrons are excited from the valence extended states to conduction extended states. As $k$ is not a good quantum number, its conservation cannot be applied in a-solids, but the momentum and energy
conservations are also applicable for transitions in a-solids. Under this condition the Fermi golden rule (Eq. (2.14)) should be written in the energy space as

$$ R = \frac{2\pi}{\hbar v} \left( \frac{e}{m^*_{e,\omega}} \right)^2 \left( \frac{E(\omega)}{2} \right)^2 |p_{cv}|^2 \sum_{E'_c, E'_v} \delta(E'_c - E'_v - \hbar \omega), \quad (2.24) $$

where the summations over $E'_v$ and $E'_c$ are to cover all states in the valence and conduction extended state, respectively, excluding any tail states. Applying the whole formulation of the c-solids presented in the previous section, we obtain

$$ \alpha = \frac{1}{nc} \left( \frac{2\pi e}{m^*_e} \right)^2 \left( \frac{1}{V \omega} \right) |p_{cv}|^2 \sum_{E'_c, E'_v} \delta(E'_c - E'_v - \hbar \omega). \quad (2.25) $$

Here it is also assumed that the matrix element is independent of the energies in the conduction and valence extended states. Now using Eq. (2.20), the double summations over energies $E'_v$ and $E'_c$ in Eq. (2.25) can be changed into double integrations as

$$ \alpha = \frac{1}{nc} \left( \frac{2\pi e}{m^*_e} \right)^2 \left( \frac{1}{V \omega} \right) |p_{cv}|^2 I, \quad (2.26) $$

where

$$ I = \int_{E_c}^{E_c + \hbar \omega} dE'_v \int_{E_c - E_v}^{E_c} g_c(E'_c) g_v(E'_v) \delta(E'_c - E'_v - \hbar \omega) dE'_v. \quad (2.27) $$

$g_c(E)$ and $g_v(E)$ are the DOS of the conduction and valence extended states, respectively. $E_v$ and $E_c$ denote the energy of the hole and electron mobility edges, respectively. Evaluating the integral in Eq. (2.27) gives

$$ \alpha = \left( \frac{e}{m} \right)^2 \left( \frac{v(m^*_e/m^*_h)^{3/2}}{\pi \hbar c \nu} \right) |p_{cv}|^2 (\hbar \omega - E_0)^2, \quad (2.28) $$

where $E_0 = E_c - E_v$ is the optical gap. We can rearrange Eq. (2.28) into

$$ (\alpha \hbar \omega)^{1/2} = \left[ \left( \frac{e}{m} \right)^2 \left( \frac{v(m^*_e/m^*_h)^{3/2}}{\pi \hbar c \nu} \right) \right]^{1/2} |p_{cv}|(\hbar \omega - E_0). \quad (2.29) $$

2.3 Tauc Band Gap

From Eq. (2.29), the dependence of the absorption coefficient on photon energy can be described as

$$ (\alpha \hbar \omega)^{1/2} = B^{1/2}(\hbar \omega - E_{\text{Tauc}}) \quad (2.30) $$

where $B^{1/2}$ is independent of the photon energy and $E_{\text{Tauc}}$ the Tauc band gap. Eq. (2.29) is a well known result first obtained by Tauc.\(^{17}\) A plot of $(\alpha \hbar \omega)^{1/2}$ as a function of the
photon energy $\hbar \omega$ is called the Tauc plot (see Fig. 4) from which the Tauc band gap can be estimated by extrapolating the linear portion to the x-axis as shown in Fig. 4.

![Figure 4. Schematic representation of the Tauc plot.](image)

2.4 Urbach Tail

Let us now consider optical transitions involving the tail states. As suggested by Urbach, in the low absorption region ($\alpha < 10^4 \text{ cm}^{-1}$), the optical absorption coefficient increases exponentially with energy following an empirical rule given by

$$\alpha \propto \exp \left( \frac{\hbar \omega}{E_U} \right)$$

(2.31)

where $E_U$ is the so-called Urbach edge energy and is related to the width of the localized tail states. The exponential tail is usually referred to as the Urbach tail. Up to now, the physical origin of the exponential behavior of the absorption coefficient is not clear. It may be caused by an exponentially increasing DOS at the band tails. It is also possible that the exponential behavior arises from the energy-dependence of the matrix element.

To summarize, a typical behavior of the absorption coefficient in the vicinity of the fundamental absorption edge is an exponential increase at the lower absorption region followed by a power law dependence (see Table 1).

<table>
<thead>
<tr>
<th>Absorption region</th>
<th>Function</th>
<th>Optical transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low ($\alpha &lt; 10^4 \text{ cm}^{-1}$)</td>
<td>Exponential</td>
<td>Between valence tail band states and extended</td>
</tr>
<tr>
<td>Urbach tail region</td>
<td>$\alpha \propto \exp \left( \frac{\hbar \omega}{E_U} \right)$</td>
<td>Between extended states in both VB and CB</td>
</tr>
<tr>
<td>High($\alpha &gt; 10^4 \text{ cm}^{-1}$)</td>
<td>Power law</td>
<td></td>
</tr>
<tr>
<td>Tauc plot region</td>
<td>$(\alpha \hbar \omega)^{1/2} \propto (\hbar \omega - E_0)$</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. A typical behavior of absorption coefficient.
Chapter 3
Method of Data Analysis

In this work, the transmission data were used to determine optical constants using the method suggested by Swanepoel as discussed in this chapter.

The transmission $T$ of a thin absorbing film deposited on a thick transparent substrate is given by

$$T = \frac{A_{x}}{B - C \cos \varphi + D x^{2}}$$  \hspace{1cm} (3.1)

where

$$A = 16 s (n^2 + k^2)$$  \hspace{1cm} (3.2a)
$$B = [(n + 1)^2 + k^2][(n + 1)(n + s^2) + k^2]$$  \hspace{1cm} (3.2b)
$$C = [(n^2 - 1 + k^2)(n^2 - s^2 + k^2) - 2k^2 (s^2 + 1)]2 \cos \varphi - k [2 (n^2 - s^2 + k^2) + (s^2 + 1) [(n^2 - 1 + k^2)]2 \sin \varphi$$  \hspace{1cm} (3.2c)
$$D = [[(n - 1)^2 + k^2][(n - 1)(n - s^2) + k^2]]$$  \hspace{1cm} (3.2d)

$$\varphi = 4 \pi n d / \lambda \quad x = \text{\texttt{exp}} (-\alpha d) \quad \alpha = 4 \pi k / \lambda \quad s = \frac{1}{T_s} + \left( \frac{1}{T_s^2} - 1 \right)^{1/2}$$  \hspace{1cm} (3.2e)

and $T_s$ is the substrate transmission.

Eq. (3.1) becomes much simpler if we put $k = 0$, an approximation that is indeed valid over most of the spectral region. Eq. (3.1) becomes

$$T = \frac{A_{x}}{B - C \cos \varphi + D x^{2}}$$  \hspace{1cm} (3.3)

where

$$A = 16 s n^2$$  \hspace{1cm} (3.4a)
$$B = (n + 1)^3(n + s^2)$$  \hspace{1cm} (3.4b)
$$C = 2(n^2 - 1)(n^2 - s^2)$$  \hspace{1cm} (3.4c)
$$D = (n - 1)^2(n - s^2)$$  \hspace{1cm} (3.4d)

$$\varphi = 4 \pi n d / \lambda \quad x = \text{\texttt{exp}} (-\alpha d)$$  \hspace{1cm} (3.4e)

The extremes of the interference fringes can be written as
\[ T_M = \frac{Ax}{B-Cx+Dx^2} \]  
\[ T_m = \frac{Ax}{B+Cx+Dx^2} \]  

Subtracting the reciprocal of Eq. (3.5a) from the reciprocal of Eq. (3.5b) yields
\[ \frac{1}{T_m} - \frac{1}{T_M} = \frac{2C}{A} \]  

Substituting Eq. (3.4) into Eq. (3.6) and solving for \( n \) yields
\[ n = \left[ N + (N^2 - s^2)^{1/2} \right]^{1/2} \]  
where \( N = 2s \frac{T_M-T_m}{T_MT_m} + \frac{s^2+1}{2} \).

Eq. (3.7) can be used to calculate \( n(\lambda) \) from \( T_M \) and \( T_m \). Once \( n(\lambda) \) is known, all the constants in Eq. (3.4) are known and \( x \) can be calculated. Both Eq. (3.5a) and Eq. (3.5b) are quadratic equations in \( x \) that can be solved for \( x \). Solving Eq. (3.5a) gives
\[ x = \frac{E_M - (n-1)^3(n^2-s^4)^{1/2}}{(n-1)^3(n-s^2)} \]  
where \( E_M = \frac{8n^2s}{T_M} + (n^2-1)(n^2-s^2) \).

Solving Eq. (3.5b) gives
\[ x = \frac{E_m - (n-1)^3(n^2-s^4)^{1/2}}{(n-1)^3(n-s^2)} \]  
where \( E_m = \frac{8n^2s}{T_m} - (n^2-1)(n^2-s^2) \).

The thickness can be calculated from the refractive indices at two adjacent maxima (or minima) using the following equation
\[ d = \frac{\lambda_1 \lambda_2}{2(\lambda_1n_2-\lambda_2n_1)} \]  

Afterwards, absorption can be calculated from \( x \) and \( d \) using Eq. (3.4e). Once the absorption coefficient is known, the extinction coefficient can be calculated from the equation \( k = a\lambda/4\pi \).

The computer program we use in this work, PUMA, calculates the optical constants from transmission data by optimizing the problem
\[ \text{Minimize } \sum_{i=1}^{N}[T(\lambda_i, s(\lambda_i), d, n_i, k_i) - T_i^{meas}]^2 \]  
where \( T(\lambda_i, s(\lambda_i), d, n_i, k_i) \) is the theoretical value of transmission calculated from Eq. (3.1) and \( T_i^{meas} \) the measured value from transmission spectra.
4.1 Fundamentals of Sputtering

Sputtering (more formally called sputter deposition) is a method of thin film deposition in which the material of a solid target is removed by energetic ion bombardment and deposited as atomic layers on a substrate. Fig. 5 shows how the impact of an atom or ion on a surface produces sputtering from the surface as a result of the momentum transfer from the incoming particle.

Figure 5. Schematics showing the momentum transfer from the incoming particle.

Figure 6. Schematics showing the sputtering process.
In the sputtering process (see Fig. 6), a plasma is created by applying a high RF or DC voltage between the target (- cathode) and the substrate (+ anode) in a vacuum chamber containing a process gas, typically Argon. To enable ignition of the plasma, the gas pressure is typically maintained in the range of 3-50 mTorr. Once the plasma is formed, gas ions in the plasma are accelerated toward the negatively charged cathode. The gas ions strike the target surface with kinetic energies up to several hundred eV and cause material to be removed (“sputtered”) from the target. Gas phase collisions between target atoms and argon atoms scatter the ejected material into a distributed cloud which migrates towards the substrate on which the film is deposited. By optimizing the distance between target and substrate, the approach angles are so randomized that a uniform film results, even on surfaces that have micron-sized vertical structures.

4.2 Sputtering Methods
4.2.1 RF Sputtering

Fig. 7a shows a schematic representation of DC-sputtering in which a negative target potential up to several kilovolts, typically -2 to -5 kV, is applied to accelerate the positively charged ions to the target. DC-sputtering is limited to conducting materials like metals and doped semiconductors. This is due to the fact that bombardment with positive ions would quickly charge up the surface of an insulating target material and cause the ion current to die off. Instead, for insulating materials, a radio frequency AC-voltage is applied to the target to prevent the charge buildup associated with DC-magnetron sputtering. This technique is called RF-magnetron sputtering. A schematic representation is provided in Fig. 7b. The oscillating rf potential applied to anode and cathode, generally operating at a frequency of 13.56 MHz, results in a modification to the electron motions, which produces better energy coupling to the electrons as well as higher plasma densities. It also leads to slightly higher deposition rates.
4.2.2 Magnetron Sputtering

An illustration of magnetron sputtering is provided in Fig. 8. A ring of magnets is placed below the target to form orthogonal $E$ and $B$ fields at the cathode surface. This results in a classic $E \times B$ drift for electrons which gives rise to a sequence of cycloidal hopping steps parallel to the cathode surface. Drifting electrons are trapped in closed loops and therefore constrained to circulate many times around the cathode surface.

The electrons follow helical paths around the magnetic field lines and therefore undergo more ionizing collisions with gaseous neutrals near the target surface than would otherwise occur. As a result of these further collisions, a higher deposition rate can be achieved. It also means that the plasma can be sustained at a lower pressure. The sputtered atoms are neutrally charged and so are not affected by the magnetic trap. In general, a magnetron discharge is much more efficient, with either DC or RF excitation, than one that does not utilize magnetic trapping.

Figure 7. Schematics of (a) DC sputtering and (b) RF sputtering.\textsuperscript{22}
4.3 Processing Pressure

Processing pressure limitations are imposed by the requirements of both glow discharge and film deposition. The glow discharge sets the lower limit. The discharge is sustained by the electrons making collision in the gas. The number of ionizing collisions will decrease with decreasing gas density or pressure. A different problem arises from high pressure. If the pressure is too high, the sputtered atoms undergo more collisions with the gas atoms on their way to the substrate. The result of the collision is to deflect the sputtered atoms and thereby decrease the deposition rate.

The trade-offs in these opposing trends lead to a need to find the optimum processing pressure for the deposition conditions. For AJA sputtering system, Ar gas pressure of 3 mTorr was found to be optimum for deposition of GeTe$_2$ films.
4.4 Description of Sputtering System

The magnetron sputtering system from AJA International is an ultra high vacuum sputter-up system with three 2" magnetron sources inside and 12" diameter and 14.6" high cylindrical stainless steel chamber (see Fig. 9). It also consists of a sample insertion load-lock chamber with a magnetic transfer arm. The Ar gas is injected from the bottom of the main chamber. In addition to Argon, Hydrogen and Oxygen can be injected to the vacuum chamber through the lamp heater assembly. The base pressure of about $1 \times 10^{-8}$ Torr is achieved by pumping the system using a turbo pump backed by a mechanical pump. The load lock vacuum is in the range of $1 \times 10^{-6}$ Torr. The main vacuum chamber is water cooled. The system can be operated in two modes of power supplies DC and RF, with maximum power outputs of 500 and 300 W, respectively. In our AJA sputtering system, one of the sputter guns is a DC-magnetron and two are RF-magnetrons. A quartz lamp based heater above the substrate holder can be used for heating the substrate up to 850 °C. The system also has the capability to apply RF-power to the substrate holder to sputter clean samples before deposition. Substrate clean processes ablate the substrate surface prior to deposition, removing organic contaminants and may also improve
adhesion through surface roughening or an increase in the surface energy of the substrate. The substrate holder can also be rotated during deposition to improve film uniformity.

4.5 Transmission Measurement Setup

A picture of the transmission measurement setup is provided in Fig. 10. The Tungsten-Halogen lamp power was set at 130 W with a PTI LPS-220 lamp power supply. The PTI 101 monochromator is a quarter-meter Czerny-Turner configuration with an f-number of 4. A 600 line/mm ruled grating made by PTI with a blaze of 1 μm and a size of 50×50 mm was installed inside the monochromator. The chopper frequency was set at 200 Hz. An AMETEK 7265 lock-in amplifier was connected to the setup. The 2mm InGaAs photodiode made by Electro-Optical Systems, INC. has an operating wavelength range of 0.8 – 1.7 μm. The computer connected to the setup uses WinReflectance software developed by Dr. Martin Muñoz.

The transmission spectrum is obtained by dividing the spectrum of the sample with the beam going through the sample by the spectrum of the lamp with the beam going directly to the detector.

Figure 10. Experimental setup for transmission measurements.
4.6 X-ray Diffractometer

Fig. 11 provides a picture of the Bruker AXS D8 Focus X-ray Diffractometer system used in our work and available in the USF Physics Department. Parameters used in XRD experiments are given in Table 2. The computer on the setup uses XRD COMMANDER software.

![Bruker AXS D8 Focus X-ray diffractometer system](image)

Figure 11. Bruker AXS D8 Focus X-ray diffractometer system.

<table>
<thead>
<tr>
<th>Table 2. Parameters of the XRD experiments.</th>
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<tr>
<td>Detector Slits</td>
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4.7 Fundamentals of Raman Spectroscopy

When light is scattered from a solid or a molecule, most photons are elastically scattered; they have the same frequency as the incident photons. However, a small fraction of photons (~ 1 in $10^7$) is scattered inelastically at optical frequencies different from the frequency of the incident photons. This scattering, known as Raman scattering,
is produced by vibrational and rotational modes of the solid or molecule. The difference in energy between the incident photon and the Raman scattered photon is equal to the energy of a vibration of the scattering solid or molecule.

4.8 Raman Spectrometer

The Raman spectroscopy measurements in this thesis were taken with a micro-Raman system, Horiba Jobin Yvon LabRAM HR, using an internal HeNe 20mW laser with a wavelength of 632.8 nm and a spot size of $2 \times 2 \ \mu m^2$. The equipment is available in the Department of Electrical Engineering and an illustration of the equipment is provided in Fig. 12. Scattered radiation is detected by a charge coupled device (CCD) detector which was calibrated using the Raman shift of a standard silicon samples as a reference. The computer on the setup uses LabSpec software.

Figure 12. Horiba Jobin Yvon LabRAM HR micro-Raman System.
5.1 Experimental Procedures

Amorphous films of GeTe$_2$ were deposited on borosilicate glass substrates at room temperature by radio-frequency (RF) magnetron sputtering at 13.56 MHz using an AJA ORION system in a sputter-up configuration. Each substrate was hand washed with acetone and methanol and blow dried with high purity nitrogen gas. The GeTe$_2$ target was supplied by AJA Int. with a purity of 99.99%.

The base pressure of the sputtering system was 2-3×10$^{-8}$ Torr and the pressure in the growth chamber during the deposition was 3 mTorr with a sputtering power of 75 W. The growth rate under these conditions was 2-3 Å/sec as recorded by the single crystal thickness monitor Maxtek TM-350. The resulting films had thicknesses of 0.6-3.0 µm. Ar and H$_2$ gas flows were controlled using mass flow controllers. The argon flow was kept at 13 sccm while the addition of H$_2$ injected into the chamber was varied between 0.5 sccm and 2.0 sccm.

X-ray diffraction results were obtained using Bruker AXS D8 Focus XRD system with scanning speed of 1 deg/min. The as-grown sample films were characterized by X-ray diffraction measurements and found to be amorphous in nature as no prominent peak was observed in the spectra. EDS measurements, performed in an Oxford INCA X-sight spectrometer, verified that the composition of deposited films was GeTe$_2$. The normal incidence transmission measurements were performed at room temperature (300 K) in the photon energy range 0.75-1.25 eV. Room temperature Raman spectroscopy measurements were taken with a micro-Raman system, LabRAM HR from JY-Horiba, using a spot size of 2×2 µm$^2$ and a 632.81 nm HeNe laser.

To investigate the crystallization temperature of GeTe$_2$ thin films, the samples prepared with various H$_2$ flow rates were annealed for 30 minutes at several temperatures
increased either until XRD patterns indicated complete crystallization or up to 500 °C. The heat treatment process was carried out under a vacuum of $10^{-6}$ Torr in order to minimize oxidation of the investigated thin films.

5.2 Results and Discussion
5.2.1 Optical Spectra

Fig. 13(a) shows the optical transmission spectra of thin films grown without and with hydrogen. The interference fringes in the plot prove the film thickness uniformity. It can be seen that the transmission spectrum shifts to a higher photon energy region with increasing hydrogen flow rate into the vacuum growth chamber during deposition. This shift can be attributed to the hydrogen present in the sample, signaling the role of hydrogen in modifying the optical properties of GeTe$_2$ films.

![Optical Spectra](image)

Figure 13. Optical spectra of GeTe$_2$ films with various H$_2$ flow rates. (a) Transmission; (b) Refractive index; (c) Extinction coefficient; (d) Absorption coefficient.
The transmission data were used to determine the optical constants (refractive index and extinction coefficient) using the Swanepoel method\textsuperscript{18, 19, 27} discussed in Chapter 3. This data analysis was done using a computer program based on unconstrained optimization\textsuperscript{28}.

Fig. 13(b) and 13(c) shows the spectral response of refractive index (n) and extinction coefficient (k), respectively, for non-hydrogenated and hydrogenated GeTe\textsubscript{2} films. The decrease of the refractive index with increasing flow rate is attributed to increasing hydrogen concentration.

The absorption coefficient can be obtained from the extinction coefficient according to the equation $\alpha = \frac{4\pi k}{\lambda}$, where $\alpha$ is the absorption coefficient and $\lambda$ is the wavelength. The results are plotted in Fig. 13(d) from which we determined the values for $E_{04}$ and $E_{03}$ in order to examine the effect of hydrogen incorporation. $E_{04}$ and $E_{03}$ are defined as the energy corresponding to absorption coefficients of $10^4$ and $10^3$ cm\textsuperscript{-1} respectively. The results are given in Fig. 14 in solid triangles.

![Figure 14. Optical gap of GeTe\textsubscript{2} thin film grown with various H\textsubscript{2} flow rates.](image)

Although $E_{04}$ and $E_{03}$ are commonly used, they do not provide further information about the structural properties of the material. For this reason, it is more favorable to use the Tauc band gap as given by\textsuperscript{29}

$$(\alpha \hbar \omega)^{1/2} = B^{1/2}(\hbar \omega - E_{Tauc})$$
where $B^{1/2}$ is the Tauc parameter, $E_{Tauc}$ is the Tauc band gap and $\hbar \omega$ is the incident photon energy. Fig. 15 shows a plot of $(\alpha \hbar \omega)^{1/2}$ versus photon energy $\hbar \omega$. The Tauc band gap can be obtained by extrapolating the linear portion of the curve to x-axis. The results are provided in Fig. 14 in circles.

The values of $E_{04}$, $E_{03}$, and $E_{Tauc}$ summarized in Fig. 15 show that the optical band gaps increase with increasing hydrogen flow rate in the growth chamber. This behavior is explained on the basis of the density of state model. According to this model, chalcogenide thin films always contain a high concentration of unsaturated bonds or defects, which are responsible for the presence of localized states in the amorphous band gap. The presence of a high density of localized states is responsible for low values of optical band gap in amorphous solids. The incorporation of hydrogen produces a large number of saturated bonds and reduces the number of unsaturated bonds, which decrease the density of localized states in the band structure. As a result, a decrease in transition probabilities occurs and leads to a consequence increase of the optical band gap.

5.2.2 Tauc Parameter $B^{1/2}$, Urbach Energy and Raman FWHM

In the Tauc model, the Tauc parameter $B^{1/2}$ is a measure of the steepness of the density of states band tail. High values of $B^{1/2}$ are due to less structural disorder.
In the low absorption region ($\alpha < 10^4 cm^{-1}$), known as the Urbach edge region, the absorption coefficient increases exponentially with energy and it is described by $\alpha \propto \exp(h\omega/E_U)$,\textsuperscript{32} where $E_U$ is the Urbach edge energy. This energy is related to the width of the localized tail states and it is considered a measure of the total disorder in amorphous materials.

Fig. 16 shows the fitting of the absorption spectrum in the Urbach region from which the Urbach energy $E_U$ was obtained for non-hydrogenated GeTe$_2$ film. For hydrogenated GeTe$_2$ films, similar fitting analysis was conducted in the Urbach region and the corresponding Urbach energies for various hydrogen flow rates were obtained.

![Figure 16. Fitting of the absorption spectrum in the Urbach region for non-hydrogenated GeTe$_2$ film.](image)

In order to correlate these two parameters, $B^{1/2}$ and $E_U$, with the network disorder, we have studied their relationship with the full width at half maximum (FWHM) of Raman modes. Raman scattering measurements provide a means of studying the lattice dynamics of disordered solids and liquids. In ordered crystalline semiconductors conservation of crystal momentum results in narrow $q \approx 0$ phonon wave-vector-associated first-order Raman scattering processes. Disorder, which arises, for example, from impurities, defects, grain size, or anharmonic effects, may modify this condition\textsuperscript{33}. It is well known that the full width at half maximum (FWHM) of the Raman peak is sensitive to various types of disorder in the film because it depends on the inverse
of phonon lifetime. Grain boundaries, impurities, and defects all decrease phonon lifetime and therefore increase the FWHM.

Fig. 17 shows the Raman spectrum of the GeTe$_2$ sample grown with 2 sccm hydrogen flow rate. The spectrum was fitted with two Lorentzian distributions using OriginLab program. Two modes were observed at 117 and 138 cm$^{-1}$ as shown by dotted lines in Fig. 17. The FWHM for each mode was obtained from the fitting results given by OriginLab. The Raman spectra of all other samples (not shown here) represent the same two modes and were analyzed in the same way as mentioned above to obtain the FWHM.

![Raman spectrum fit](image1)

Figure 17. Raman spectra of amorphous GeTe$_2$ thin films and the fitting with two Lorentz distributions.

![Graph](image2)

Figure 18. Plot of Raman FWHM and Urbach edge energy versus Tauc parameter.
The top part of Fig. 18 shows a plot of the Urbach edge energy versus the Tauc slope $B^{1/2}$ parameter. The middle and the bottom part of the Fig. 16 correspond to the FWHM of the peaks at 117 and 138 cm$^{-1}$, respectively, as a function of the $B^{1/2}$ parameter.

According to Fig. 18, the introduction of hydrogen (flow rate $< 2.0$ sccm) into the amorphous GeTe$_2$ increases the network disorder, the Urbach edge energy $E_U$ and the FWHM of Raman modes, while it decreases $B^{1/2}$. Moreover, the straight lines shown in this figure indicate a linear relationship between $E_U$, $B^{1/2}$ and the FWHM of Raman modes.

5.2.3 Annealing Effect on Optical Transmission

The crystallization process and its effects on the optical and electrical properties of chalcogenide materials are important in applications such as information storage by either optical or electrical means. We have studied the crystallization process of the GeTe$_2$ films as a function of the annealing temperature and flux of H$_2$ in the chamber during the deposition process.

Fig. 19a and 19b show the transmission spectra of GeTe$_2$ film, grown under 0 sccm and 1 sccm flux of H$_2$ respectively, before annealing and after complete crystallization. It can be easily seen that these two GeTe$_2$ films have extremely low transmission in the spectral region 0.75-1.25 eV after amorphous-crystalline transformation. This great reflectance contrast in the spectral region 0.75-1.25 eV after phase change was also observed for other hydrogenated and non-hydrogenated GeTe$_2$ samples (not shown here). For the GeTe$_2$ film grown with the highest H$_2$ flow rate (2 sccm), the transmission spectrum (see Fig. 19c) remains the same as the one before annealing because the substrate softening temperature does not allow us to attain the crystallization temperature in this case. This agrees with the (XRD) results which shows that the film does not crystallize at temperatures lower than 500 °C.
5.2.4 XRD Characterization

In order to investigate the details of the crystalline phase producing the large reflectivity contrast, XRD studies were performed and the results are provided in Fig. 20.

Fig. 20a shows the XRD spectra corresponding to non-hydrogenated GeTe$_2$ film. It can be seen that the sample completely crystallizes at 350 °C.

Fig. 20b suggests that the sample grown with 1 sccm H$_2$ flow rate remains amorphous up to 300 °C and partially crystallizes by increasing the annealing temperature from 350 to 400 °C, as indicated by the intensity increase of the peaks at 23 and 30°. The complete crystallization is monitored by tracking whether or not significant...
changes in the peaks intensity is occurring and therefore is determined to occur between 450 and 480 °C.

It is easily seen from Fig. 20c that the GeTe$_2$ film grown with 2 sccm hydrogen flow rate doesn’t crystallize at temperatures lower than 500 °C since there are no prominent crystalline peaks observed. No higher temperatures are investigated due to the limitations imposed by the substrate softening temperature (550 °C).

Figure 20. XRD results for GeTe$_2$ films grown (a) without hydrogen, (b) with 1 sccm and (c) 2 sccm hydrogen flow rate.

According to all the above figures, the crystallization temperature of GeTe$_2$ films increases with increasing hydrogen flow rate in the growth chamber. This increase in crystallization temperature is interpreted in terms of dangling bonds. The incorporated hydrogen atoms in the films reduce the density of dangling bonds available for reengagement during the crystallization and hence increase the crystallization
temperature. Therefore, as hydrogen concentration increases, crystallization temperature shifts to a higher temperature.

Analysis of the XRD spectra in Fig. 20 reveals a phase separation during the crystallization process. The phase separation in GeTe$_2$ system occurs because crystalline GeTe$_2$ does not exist$^{34}$ and only one Te atom is required for GeTe phase and the other Te atom is left to form an elemental phase. The identified crystalline phases are the following: (i) Te phase with hexagonal structure of unit cell constants $a=4.445$ Å and $c=5.910$ Å and (ii) GeTe rhombohedral structure of lattice constants $a=8.427$ Å and $c=10.710$ Å. These unit cell constants are in agreement with previous reports.$^{35}$ Crystalline GeTe and Te have optical gaps of 0.2 eV and 0.335 eV respectively,$^{14,36}$ and hence strong absorption in the spectral range 0.75-1.25 eV. Due to this reason, great transmission decrease is observed after the amorphous-crystalline transformation as shown in Fig. 19.
Chapter 6
Conclusions

The work in this thesis presented the effect of hydrogen incorporation on the optical properties and crystallization temperature of sputtered GeTe$_2$ films. The optical gaps ($E_{04}$, $E_{03}$ and $E_{\text{Tauc}}$), Urbach energy $E_U$ and FWHM of Raman modes increase while the Tauc parameter $B^{1/2}$ decreases with increasing hydrogen flow rate from 0.5 sccm to 2 sccm. According to the FWHM of Raman modes, the inclusion of hydrogen atoms into the amorphous GeTe$_2$ network produces more disorder. There have been observed linear relationships between the Raman FWHM, $B^{1/2}$ and $E_U$. Our investigated non-hydrogenated GeTe$_2$ films have a crystallization temperature of 350 °C. The crystallization temperature shifts to a higher temperature with increasing hydrogen flow rate in the growth chamber because the incorporated hydrogen atoms reduce the density of dangling bonds available for the network rearrangement. Phase separation has been observed in both non-hydrogenated and hydrogenated GeTe$_2$ films. The identified crystalline phases are hexagonal structure Te phase and rhombohedral structure GeTe phase. After amorphous-crystalline transformation, both non-hydrogenated and hydrogenated GeTe$_2$ films experienced great transmission decrease (~60%) in the spectral region 0.75-1.25 eV due to the narrow band gaps of the constitutive crystalline phases.
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