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Chalcogenide-Based Phase-Change Metamaterials

by

Jonathan S. Maddock

Thesis for the degree of Master of Philosophy

August 2014
Phase-change metamaterials combine the sharp resonant dispersions afforded by metamaterials with the optical switching characteristics of phase-change chalcogenides to create a high-contrast, non-volatile planar optical modulator. Spectroscopic ellipsometry was used to accurately determine the highly-contrasting complex dielectric functions of the amorphous and crystalline states of GST, an amorphous chalcogenide. This data was then used to model a phase-change metamaterial hybrid device in both phases, which showed a large wavelength shift in resonant spectral features on crystallisation of the chalcogenide layer. Femtosecond pulse-induced crystallisation and amorphisation of thin films of GST was shown to be possible, and the crystalline fraction in the material was shown to be continuously tunable. Femtosecond pulses were then used to reversibly switch a phase-change metamaterial device to modulate the trapped mode resonance. Modelling of an all-dielectric phase-change metamaterial structure indicated that larger optical modulation may be realised by changing the phase of the resonant structure itself.
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Declaration of Authorship

I, Jonathan S. Maddock, declare that the thesis entitled *Chalcogenide-Based Phase-Change Metamaterials* and the work presented in the thesis are both my own, and have been generated by me as the result of my own original research. I confirm that:

- this work was done wholly or mainly while in candidature for a research degree at this University;
- where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated;

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• where I have consulted the published work of others, this is always clearly attributed;

• where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work;

• I have acknowledged all main sources of help;

• where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself;

• none of this work has been published before submission

Signed:.....................................................................................................................

Date:.....................................................................................................................

28.4.14
Acknowledgements

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Chapter 1

Introduction

1.1 Introduction to Phase-Change Metamaterials

Phase-Change Metamaterials (PCMMs) are an amalgamation of two existing material concepts to provide new optical functionalities in a single device (see Figure 1.1). The phase-change layer is typically a chalcogenide glass that can be thermally switched between two phases: crystalline and amorphous. The layer will remain in either of these states until it is switched again, providing a ‘memory’ effect. The metamaterial layer consists of repeating subwavelength unit cells of Asymmetric Split Rings (ASRs) milled from a thin layer of plasmonic material, such as gold. Such a layer will produce sharp resonance peaks in transmission or reflection when illuminated with a particular wavelength\[1.1\].

The combined device creates a tunable metamaterial with memory that can be switched into different states through thermal crystallisation or amorphisation of the phase-change layer. The device has applications as a high-speed electro-optical or all-optical light modulator of tunable wavelength and with a memory of its previous state\[1.2\].

Figure 1.1: A phase-change metamaterial device structure.
1.2 Motivation

Phase-change materials display excellent modulation contrast; many of their properties can change dramatically between two extremes with minimal energy input[1.3]. Together with the fact that this change can occur very rapidly makes phase-change materials not only attractive for information storage applications but also in active devices, such as logic gates and switches. The novel order-disorder transition present in many chalcogenide glasses results in unique switching properties such as high speed and low energy consumption per switch.

Metamaterials are an exciting new paradigm in photonics that concerns the interaction of light with materials patterned on the sub-wavelength scale, exploiting surface plasmon resonances[1.4]. These materials were largely inspired by microwave frequency selective surfaces, and can have optical characteristics that are otherwise impossible in conventional materials.

One problem of great current importance in optical communications is how to reduce the ‘electronic bottleneck’ caused by the requirement to convert transmitted optical signals to electronic signals for processing and back again for further transmission. There is therefore a significant performance gain to be made from all-optical data processing. To realise this, compact, rapid and high modulation contrast active devices need to be produced that can change their refractive index and absorption[1.4].

Such a device could be created through combining the attributes of phase-change materials and metamaterials, and it may provide a platform for non-volatile all-optical memory, logic and data processing. As the crystallinity of the phase-change layer is varied continuously from a fully amorphous to a fully crystalline phase, a progressive shift in the resonance of the adjacent metamaterial layer can be produced. Due to the non-volatility of the phase-change material, successive switching events can be ‘remembered’ and accumulated. This gives rise to a ‘cumulative’ switching effect in the spectral resonance features of the metamaterial, raising the possibility of some form of optical logic and information processing in such a device.

The original contribution of this research is to create a phase-change metamaterial device that can be crystallised and amorphised using femtosecond pulses, to create a femtosecond-actuated high-contrast optical modulator. Continuous tuning of the crystalline fraction in thin films of GST was achieved using femtosecond-timescale optical pulses, showing continuous modulation is also possible. Modelling of an all-dielectric phase-change metamaterial promises improved resonance modulation on optical switching.
1.3 Aims

The primary aim is to develop an all-optical phase-change metamaterial active device which is non-volatile, tunable and cyclable (i.e. survives successive operations). The device will initially serve as a bistable switch to modulate the trapped mode resonance in the metamaterial, but will be developed to demonstrate more advanced functionality such as progressive tuning and accumulation operations. Femtosecond pulse-induced crystallisation will be investigated, as will new metamaterial structures incorporating switchable chalcogenides.

1.4 Objectives

- Obtain accurate dispersions for thin films of GST through ellipsometry, and how these vary as the glasses move from the amorphous through to the crystalline phase
- Fabricate and characterise a well-understood metamaterial pattern to measure the stand-alone metamaterial response of the structure
- Successfully optically switch (change phase from amorphous to crystalline and back) thin films of GST, and optimise laser parameters to minimise damage and maximise contrast between the two states
- Demonstrate GST switching induced via femtosecond optical pulses
- Model the hybrid phase-change metamaterial device to optimise design parameters for maximum optical contrast between the amorphous and crystalline states
- Fabricate a phase-change metamaterial, and characterise the optical response in both phases
- Optically switch the PCMM into intermediate states, to provide progressive tunability between the two extremes of fully amorphous or crystalline
- Create a pixellated PCMM in which logic and information processing might be conducted
- Model an all-dielectric phase-change metamaterial and investigate its switching functionality

1.5 Layout of Report

The report begins with some background on chalcogenide glasses and their structure, before focussing on chalcogenides as phase-change materials and the mechanisms of
phase-change. Metamaterials are then introduced along with some of their unique properties and applications. The two fields are then brought together to explain phase-change metamaterials and some of the prior work that has been done on them.

Spectroscopic ellipsometry studies are then presented to provide accurate dispersions for all materials used in the final device; this is crucial for the modelling of the hybrid device in the following section. All-dielectric phase-change metamaterials are then modelled to investigate their viability as a switchable metamaterial platform. Femtosecond-timescale excitation of GST thin films is then investigated, along with femtosecond pulse-induced crystallisation of PCMMs. Finally conclusions of this work are presented.

References


Chapter 2

Phase-Change Materials

2.1 Chalcogenide Glasses

2.1.1 Properties of Chalcogenide Glasses

Chalcogenides are compounds formed at least in part from the chalcogens in group 16 of the periodic table; typically sulphur, selenium and tellurium (although oxygen is not considered a chalcogenide). Certain compositions are good glass-formers, which display a high transparency in the mid-infrared and also offer many active properties, such as semiconductivity and high nonlinearity\[2.1\][2.2]. High nonlinearity, combined with a variety of photo-induced effects, makes these materials promising for active devices; for example, all-optical femtosecond switches\[2.3\]. The materials can be fabricated in a range of different forms such as thin films, microspheres and optical fibres\[2.4\]. Current applications include optical data storage and solar cells.

Binary chalcogenide compounds typically consist of a chalcogen and an element from either group 14 or 15, but additional elements can be added to these to form ternary compounds\[2.4\]. Chalcogens have the outer electron configuration ns²np⁴, where n is the principal quantum number. Of the 4 electrons in the outermost p orbital, only 2 are used to form covalent bonds with neighbouring atoms\[2.5\]. This leaves two electrons in the p orbital, a lone pair, which forms the top of the valence band. This lone pair introduces a flexibility to the material, which is a useful characteristic, as many free carriers in the glass may be excited without breaking any bonds or reducing structural integrity\[2.6\]. Crystallisation and amorphisation of chalcogenides offers a near-step change in optical and electrical properties upon different conditions of thermal excitation. Chalcogenides exhibit large and rapid changes in electrical and optical properties via electrical or optical excitation; they are therefore a crucial material system in optoelectronics.
2.1.2 Structure of GST

The structure of Ge$_2$Sb$_2$Te$_5$ (GST) is fundamental to its unique properties which make it so useful as a phase-change material. Stable bulk crystalline GST is known to possess the hexagonal structure\[2.7\]. However thin films of laser-crystallised GST have been shown to possess a ‘rocksalt’ structure; Te atoms form one face-centered cubic (FCC) sublattice, whilst Ge and Sb randomly occupy the lattice sites in an interlocking FCC sublattice to form the rocksalt structure\[2.8\]. 20% of these second sublattice sites are believed to be vacant. The amorphous phase is complex, with different ranges of order (a thorough discussion is offered by Elliott\[2.9\]), but can be coarsely approximated to the random rocksalt structure. As only the thin film crystalline-amorphous case is of interest here, the rocksalt structure specific to GST will be discussed in more detail.

The electron configurations of the constituent elements of GST are given in Table 2.2.

In the crystalline octahedral state, each atom has 6 neighbours, and hence 6 covalent bonds. As there are not enough electrons to satisfy Mott’s 8-N rule for each atom, resonant bonds form\[2.10\]. These resonant bonds can only form when the p-orbitals of neighbouring atoms align. In the amorphous phase, there is no long-range order, and hence no alignment of p-orbitals and no resonant bonding. The presence of resonant bonding in the crystalline material helps explain the contrast in refractive index between the two phases; resonant bonding between atoms results in an increase in polarisability in the material, and hence an increase in the refractive index.

Kolobov et. al. explain the material as having a ‘distorted rocksalt’ type structure, where due to covalent radii differences between the 3 species, Ge, and to a less extent Sb, atoms are displaced from their ideal FCC positions in a ‘buckled’ structure consisting of varying bond lengths\[2.8\]. This is also due to charge redistribution between constituent elements. The shorter bonds produced are stronger, and hence provide a ‘rigid framework’ for the local structure.

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In real-world crystals, on a long-range scale, Ge and Sb atoms may be randomly allocated in their sublattice. Further, each GST unit may rotate by 90° in an arbitrary direction.

<table>
<thead>
<tr>
<th>Element</th>
<th>Electron Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>[Ar]3d$^{10}$4s$^2$4p$^2$</td>
</tr>
<tr>
<td>Sb</td>
<td>[Kr]4d$^{10}$5s$^2$5p$^3$</td>
</tr>
<tr>
<td>Te</td>
<td>[Kr]4d$^{10}$5s$^2$5p$^4$</td>
</tr>
</tbody>
</table>

Table 2.1: Electron configurations of the constituent elements of GST.
Chapter 2 Phase-Change Materials

Figure 2.1: The structure of GST in a laser-crystallised thin film: a cross-section of the distorted rocksalt structure showing Te-Ge and Te-Sb bonds, together with vacancies. The thick lines denote strong bonds, which form a ‘unit’ of GST. (Figure reproduced from [2.8])

Figure 2.2: The ‘umbrella flip’ structural transformation in GST. The Ge atom (shown in red) is octahedrally coordinated in a FCC lattice of Te atoms (shown in green). The Ge atom ‘flips’ from an octahedral coordination (crystalline) (a) to a tetrahedral coordination (amorphous) (b) in a bistable fashion, similar to an umbrella on a windy day. In this model, the Te sub-lattice moves very little during the transformation; it is not truly amorphised. The orange plane, drawn between three Te atoms, is solely to guide the eye. (Figure reproduced from [2.8])

The model in Figure 2.1 is useful in explaining an interesting property of GST. On amorphisation, the intermolecular (longer Te-Ge and Te-Sb) bonds are broken, resulting in a shortening and hence strengthening of the intramolecular (shorter Te-Ge and Te-Sb) bonds. This results in higher local order in the amorphous phase than the crystalline phase, even though there is little long-range order.

The ‘umbrella flip’ of a Ge atom in the Te FCC structure could help explain the unique phase change properties of GST. A crystallising laser pulse breaks the longer Te-Ge bonds which causes the Ge to move slightly, causing the Ge to go from an octahedral
(crystalline) to its preferred tetrahedral (amorphous) coordination, thus creating disorder in the Ge sublattice\cite{2.11}. The stronger Te-Ge covalent bonds are maintained, as they only have their angles shifted; only the weaker bonds are broken, and the material never truly melts. This novel order-disorder transition makes the phase change event fast, efficient and bistable, much like an umbrella turning inside-out.

The structural transformations appear to pivot around the Sb ‘scaffolding’, and the Te movements are very slight as well. The fact that in the amorphous state the local structure is highly ordered results in the transformation being more easily reversible, as the total atomic position changes are very slight, with the Ge umbrella flip being the most dramatic. In the amorphous phase, the resonant metallic bonding state is terminated, resulting in a dramatic change in electronic and optical properties.

The longer Te-Ge bonds are weaker, and hence have lower-energy densities of states. A laser pulse will produce ‘photogenerated nonequilibrium carriers’ which can populate these states, thereby weakening the bond and facilitating bond dissociation due to thermal vibrations\cite{2.8}. This may be the mechanism of ‘photocrystallisation’. Additionally, if the incident laser pulse is to be dissipated non-radiatively, then phonons must be produced. This requires states in the bandgap; regions in the material that provide these states will have more phonons produced at those locations, and therefore will be selectively heated. This can produce regions where the heat is ‘focussed’. These two mechanisms provide lower-energy paths for crystallisation, which would otherwise necessitate the much higher temperature of the onset of crystallisation to be obtained.

GST provides an excellent case-study for phase-change materials, as many of the structural concepts it illustrates can be echoed by other materials with good phase change properties.

### 2.1.3 Structure of GLS

Gallium Lanthanum Sulphide (GLS) glass was originally of interest due to its high solubility of rare earth elements (such as Er) and long characteristic lifetimes of their excited states within this matrix\cite{2.12}. Recently, it has been identified as another glass of particular interest in phase-change research; GLS can display fast switching, has a high glass transition temperature (making it thermally stable and unlikely to ‘drift’ with time like GST) and furthermore its components are non-toxic\cite{2.4}.

GLS has a different structure to other chalcogenides, hence it is referred to as $\text{Ga}_2\text{S}_3$-$\text{La}_2\text{S}_3$. The $\text{Ga}_2\text{S}_3$ component is the conditional glass former, but requires a glass modifier, $\text{La}_2\text{S}_3$, to form a glass\cite{2.13}. The structure consists of tetrahedral covalent GaS$_4$ units, which are very similar to those found in crystalline GaS$_4$\cite{2.14}. The La$_2$S$_3$ forms ionic channels throughout the structure, which break up the GaS$_4$ network. GLS
Figure 2.3: The structure of the covalent crystalline Ga$_2$S$_3$ network. The lines joining atoms represent covalent bonds, and the arrows represent dative bonds. Reproduced from [2.15].

can be said to follow a Modified Random Network (MRN) structural model, and a typical glass-forming composition might be 70Ga$_2$S$_3$-30La$_2$S$_3$.

<table>
<thead>
<tr>
<th>Element</th>
<th>Electron Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga</td>
<td>[Ar]4s$^2$3d$^{10}$4p$^1$</td>
</tr>
<tr>
<td>La</td>
<td>[Xe]5d$^1$6s$^2$</td>
</tr>
<tr>
<td>S</td>
<td>[Ne]3s$^2$3p$^4$</td>
</tr>
</tbody>
</table>

Table 2.2: Electron configurations of the constituent elements of GLS.

The electron configurations of the constituent elements of GLS are given in Table 2.2. In a Ga$_2$S$_3$ crystal (shown in Figure 2.3), 3 S atoms are bonded to 3 Ga atoms each; each S atom maintains 2 covalent bonds and a third dative bond. The 4th S atom is covalently bonded to 2 Ga atoms, and acts a bridging atom; resulting in GaS$_4$ tetrahedra bridged together to form the Ga$_2$S$_3$ crystalline structure. These ‘bridged’ tetrahedra form the backbone of the glass network[2.16].

Adding La$_2$S$_3$ brings in a S$^{2-}$ anion, which ruptures the Ga-S dative bond in the Ga$_2$S$_3$ structure. This results in a tetrahedral GaS$_4$ unit, with a negative S$^{2-}$ site for the La$^{3+}$ cation to bond to[2.13]. This results in ‘Ga$_4$ tetrahedra intercalated with ionic La-S channels’, each displaying medium-range order, as shown in Figure 2.4[2.15].

It has been noted that there is considerable disorder in Ga-S bond length, but little in the La-S bond length[2.17]. Ga is tetracoordinated in both glassy and crystalline states, and the Ga-S bond length does not noticeably change between the two states, but the La-S distances are slightly more dispersed in the amorphous case[2.15]. If there
is only a Ga-S bond angle change between the two states, it can be put forward that the phase-change transition in GLS will be rapid. If GLS can be shown to possess similar phase-change characteristics to GST (e.g. thresholding), then this could be indicative of a more intricate mechanism of phase-change between the amorphous and crystalline states, as with GST.

When synthesising bulk GLS, as the glass transition temperature and the crystallisation temperature are so close, unwanted crystallisation frequently occurs, preventing the formation of a vitreous system[2.4]. Therefore it is necessary to add a network stabiliser such as lanthanum oxide (La$_2$O$_3$), which inhibits crystallisation in the glass melt. For phase-change GLS, lanthanum oxide can be added to the system to raise the crystallisation temperature; the crystallisation event will be slower and require more energy, but amorphisation quench times can afford to be slower; it allows the melt to be quenched into the amorphous state. Conversely, no oxide GLS will result in a fast crystallisation, but the system will have to be quenched back to the amorphous state more rapidly. The balance of glass formers (GaS$_4$), network modifiers (La$_2$S$_3$) and network stabilisers (La$_2$O$_3$) determines whether the GLS displays fast crystallisation or high thermal stability, a common trade-off in phase-change materials.

2.1.4 Glass Fabrication

2.1.4.1 Melting

Traditionally, chalcogenides were synthesised using sealed ampoule melting. The precursors are batched under nitrogen and then sealed under vacuum in a silica ampoule.

![Figure 2.4: The structure of Ga$_2$S$_3$-La$_2$S$_3$ (GLS) glass. Reproduced from [2.15].](image-url)
and melted and quenched. The reasoning behind this method is that many of the precursors used to synthesise chalcogenides are volatile, and would either react with the atmosphere or vaporise completely; the sealed ampoule method ensures no (or very little) compositional change during the melt. However, the final glass is only as pure as the precursors; this is the limiting factor in the resulting glass purity[2.4].

Open atmosphere melting was used in the early days of chalcogenide synthesis, mostly due to the explosive nature of sulphur reactions. However, this process resulted in huge compositional variations from melt to melt, and was environmentally ill-advised[2.4]. GLS glass lends itself particularly well to the open-atmosphere method, however, as the precursors (Ga$_2$S$_3$, La$_2$S$_3$ and La$_2$O$_3$) are all comparatively non-volatile. The precursors are batched in a nitrogen-purged glovebox, transferred to a vitreous carbon crucible and melted in a silica tube furnace in a sealed vessel under flowing argon. Typical melt parameters could be 1150°C for 23 hours, then 1050°C for 1 hour, before being quenched in a water jacket. This method allows for any impurities to vaporise and be taken away with the exhaust, resulting in purification and melting at the same time, a significant advantage over the sealed ampoule system.

2.1.4.2 Thin-film deposition

Sputtering is used to deposit thin films of chalcogenides as it can produce excellent quality films (highly uniform in thickness and composition) whilst maintaining the composition of the original target in the deposited film. It also can be performed at room temperature. Some targets (such as GST) are commercially available, but GLS targets are hot-pressed in-house from crushed glass; whilst this produces crystallised GLS targets, the resulting sputtered films are amorphous. Targets can also be made simply by cutting a glass melted in a crucible of the same dimensions as the desired target.

The material is then deposited from the target as a thin film using a Kurt J. Lesker Nano 38 RF magnetron sputtering machine, typically depositing thicknesses on the nanometre scale on a variety of substrates. A substrate is selected based on the optical characterisation required of the finished device (optimal for NIR, MIR etc.; borosilicate glass, microscope coverslip, CaF$_2$ or fused quartz). A phase-change layer of 50 nm GST (for example) is sputtered using a base pressure of 9.00 × 10$^{-5}$ Torr or lower, an argon flow rate of 35 cc min$^{-1}$ and a gun forward power of 35 W. A ZnS-SiO$_2$ capping layer is necessary to prevent the GST from reacting with the oxygen in the atmosphere. A typical capping layer of 30 nm ZnS-SiO$_2$ is then sputtered to prevent oxidation of the phase-change material, using a base pressure of 9.00 × 10$^{-5}$ Torr or lower, an argon flow rate of 35 cc min$^{-1}$ and a gun forward power of 70 W.
Additionally, Chemical Vapour Deposition (CVD) can be used to create thin films on non-planar surfaces. Structures and devices can then be fabricated using conventional photolithographic techniques.

2.2 Phase-Change Materials

2.2.1 The Phase-Change Transition

Phase-change materials are so-called because they can be made to transform between two metastable phases: the amorphous and crystalline states (see Figure 2.5). This is usually achieved by heating at different temperatures and rates. If the material is initially in the amorphous state, heating it slightly above the glass transition temperature \( T_g \) will increase the atomic mobility. Heating above \( T_x \), the crystallisation temperature, will allow the atoms to find a lower energy configuration; they will begin to form a crystalline structure[2.19]. When the heating is stopped, the atoms will remain in this configuration. If the material is heated above its melting temperature \( T_m \), then the atoms will re-amorphise as the material enters the liquid phase. Rapidly removing the heating from the liquid material will cause it to cool rapidly, and this melt-quench process will cause the disorder to be ‘frozen’ into the solid material, so that the amorphous state is obtained again.

![Figure 2.5: The phases of glass. The red arrow denotes crystallisation on slow cooling of the liquid phase; the glass will be cooled to the crystalline phase. If the liquid is cooled sufficiently rapidly, it forms its amorphous phase; the blue arrow denotes the path of the crystallisation process when the glass is taken above its \( T_g \) to \( T_x \) and crystallised from the amorphous phase. Figure adapted from [2.18].](image-url)
Figure 2.6: The phase transition in phase-change materials, as a result of electrical or optical excitation. A low-power (set) pulse ensures a high enough temperature to overcome $T_x$ and the material crystallises. A high-power (reset) pulse increases the temperature above $T_m$ to melt the crystalline material before abruptly ending to quench the liquid back to the amorphous solid state [2.19]. Figure adapted from [2.18].

The heating is either performed electrically via Joule heating or optically using a laser. A ‘set’ operation consists of a relatively long, low power pulse resulting in an amorphous to crystalline transition in the material. A ‘reset’ operation consists of a shorter, higher power pulse resulting in a crystalline to amorphous transition in the material. The corresponding changes in electrical and optical properties properties are shown in Figure 2.6.

One of the reasons that phase-change materials are so attractive is that the phase transition causes dramatic changes in both the electrical regime (resistance) and the optical regime (reflectivity and transmission). This means that not only can both regimes be used to probe the material in question, but both regimes may also be used to control the device. Phase-change materials hence open exciting new possibilities in optoelectronics, as the same material can strongly interact with both regimes.


2.2.2 Nucleation and Growth

Phase-change materials with different compositions fall into two categories: those which are nucleation-dominated and those which are growth-dominated[2.20]. In the case of nucleation-dominated materials, the nucleation probability density is high relative to the growth probability density, and as a result nucleation occurs significantly at a lower temperature than growth, so nuclei will form and then growth will occur at those nucleation sites; the material will crystallise throughout, with the crystalline nuclei growing until they coalesce. In the case of growth-dominated crystallisation, the probability of nucleation is relatively small compared to that of growth, so the crystallisation occurs at an existing amorphous-crystalline interface, which then moves as the material crystallises further[2.21, 22].

Most successful phase-change materials lie on the pseudobinary line between GeTe and Sb$_2$Te$_3$, having the composition (GeTe)$_m$(Sb$_2$Te$_3$)$_n$[2.23, 24]. The crystallisation of GeSbTe is nucleation-dominated, but doped SbTe is growth-dominated[2.20].

2.3 Phase-Change Work

2.3.1 Fabrication

Thin films of GST and GLS were successfully sputter deposited on a variety of substrates (borosilicate, fused quartz and CaF$_2$) with good surface uniformity and roughness (within ±10% of the total thickness deposited). The deposition thickness was monitored during deposition using a quartz crystal oscillator in the sputtering chamber, and the thickness was checked using a KLA-Tencor P-16 stylus profiler and a Zemetrics ZeScope white-light interferometer. The typical fabrication steps were as follows:

1. A quartz substrate was sonicated with acetone, isopropanol and de-ionised water to remove any surface particulates

2. 30 nm of the phase-change layer was sputtered onto the substrate

3. 10 nm ZnS/SiO$_2$ (of composition 80:20) was then sputtered on top without breaking vacuum to prevent oxidation of the phase-change material.

2.3.2 Optical Switching

Of the two methods of switching phase-change materials, optical switching is much simpler for fabrication purposes, and can be performed on a thin film without any need for electrodes or contacts. A focussed Continuous Wave (CW) or pulsed laser was
Figure 2.7: The optical switching setup. The laser used was a 405 nm 120 mW laser diode from Mitsubishi (ML320G2-11), and the objective was a Nikon 20x lens. The stage could be scanned in the x and y directions (perpendicular to the incident beam) to rapidly switch multiple areas. The transmission lamp allows higher-contrast inspection of the crystallised spot using the CCD than could be produced in reflection.

applied normal to the film using the setup shown in Figure 2.7, and the heat generated as a result of the absorption in the film resulted in a phase-change event. For this work, an uncapped 100 nm GST film on a 50 mm × 50 mm borosilicate slide was used. 405 nm was used as many chalcogenides absorb strongly at this wavelength, and therefore crystallising the film is possible with lower intensities.

The nature of the phase-change event in a chalcogenide thin film depends on the local temperature of the film, as well as the time-dependency of the temperature change. In the simplest case, we consider a CW laser incident normally on the film, which is maintained in dynamic thermal equilibrium. If the laser profile is assumed to be Gaussian, in the CW thermal equilibrium case, then only the central portion of the spot will raise the temperature of the thin film above the crystallisation threshold. A schematic of a typical laser-crystallised spot in a phase-change thin film is shown in Figure 2.8, and a brief description of each region is given in Table 2.3. This gives an indication of some of the typical regions identifiable in an experimental switching event; the actual presence and size of the regions depends on laser intensity, pulse duration, beam profile and the crystallisation kinetics of the chalcogenide.
Chapter 2 Phase-Change Materials

Amorphous
Sub-threshold
Crystallisation threshold
Ablated

Partially crystallised
Fully crystallised

Figure 2.8: A diagram of typical regions expected in a laser-crystallised mark in an amorphous phase-change film when switched with a Gaussian-profile beam.

<table>
<thead>
<tr>
<th>Region</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous</td>
<td>Amorphous, disordered, as deposited film</td>
</tr>
<tr>
<td>Sub-threshold</td>
<td>Some ordering, but largely immeasurable optically</td>
</tr>
<tr>
<td>Crystallisation threshold</td>
<td>The film has reached $T_x$; significant, optically discernable structural ordering</td>
</tr>
<tr>
<td>Partially crystallised</td>
<td>An intermediate volume fraction of crystallinity has been achieved</td>
</tr>
<tr>
<td>Fully crystallised</td>
<td>The crystalline volume fraction tends to unity</td>
</tr>
<tr>
<td>Ablated</td>
<td>The chalcogenide has exceeded $T_m$ and a portion of the film has evaporated</td>
</tr>
</tbody>
</table>

Table 2.3: Descriptions of various regions of structural order in a laser-crystallised spot.

This is obviously a greatly simplified picture; it has been assumed that the intensity of the incident radiation is directly proportional to the heating effect in the film, and that there is no lateral diffusion of heat along the plane of the film. It is also assumed that static temperature is the only variable affecting crystallisation. The real situation is somewhat more complex; an example of experimental optical switching is given in Figures 2.9 and 2.10.

To produce these pulse number against pulse power arrays, a program was developed in Labview to automatically move the stage and deliver the correct number of pulses. The program was designed to be modular, so that instead of operating a shutter for a CW diode laser, it could trigger a femtosecond pulse picker for a single-shot fs pulse, or modulate pulse duration across the array instead of pulse number, for example. The program provided a way of rapidly sweeping optical switching parameter spaces, which would be tedious and prone to error if performed by hand. It also can be used to raster scan an area to reliably produce uniform crystallisation across that area.
Figure 2.9: An array of optically-switched crystallised spots in a 100 nm thick film of GST on a borosilicate slide, with varying pulse power and number of pulses. Each ‘pulse’ was gated using a mechanical shutter which would open to allow 100 ms of 405 nm light at various intensities to pass through the objective and onto the sample. The shutter would then close for 100 ms before the next pulse, with a quoted timing accuracy of ±10 ms. The image was taken on a microscope in transmission mode; the light areas in the middle of the marks correspond to regions of ablated film.

Figure 2.10: A close-up of optically crystallised spots from Figure 2.9, again imaged in transmission. The top-left and top-right marks were produced by 7 and 8 27 mW pulses respectively, and the bottom-left and bottom-right marks were produced by 7 and 8 24 mW pulses respectively. The internal structure in each mark is more visible here. The central ablated region appears to be consistently asymmetric; this could be due to poor beam quality.
Chapter 2 Phase-Change Materials

Figure 2.11: Average mark nature in an optically-switched array: pulse power against number of pulses. The average nature of each mark was estimated as a function of position in the pulse power and number of pulses space.

Key regions given in Figure 2.8 can be seen in each crystallised spot in Figure 2.10. Moving radially outwards from the centre of each spot, the following regions can be seen: the light central ablated region, then an abrupt change to a dark fully crystalline region, getting slightly lighter as the radius increases, indicating a decreasing crystalline fraction, and finally an abrupt change to the sub-threshold ordered or amorphous region.

To get the highest optical contrast in transmission or reflection between any two states, it is necessary to switch the material between its two structurally most different phases, fully amorphous and fully crystalline, without ablating the film. This is possible, but due to the Gaussian intensity profile of the beam, there will always be a gradient of temperature (and indeed temperature history) as one moves radially outwards from the center of the mark.

It should be noted that whilst GST films have been crystallised, they have not been successfully amorphised in this chapter. This is due to the pulse parameters for optical amorphisation needing to be much more specific, and the quench rate needing to be sufficiently rapid. The necessary parameters could not be found to achieve amorphisation in the GST film using the 405 nm diode laser, even with nanosecond-timescale pulse durations to maximise the quench rate, and hence the likelihood of formation of the amorphous phase.

2.3.3 Pre-Threshold States and Multi-Level States

Ovshinsky, one of the pioneers of phase-change memory, has often discussed the capabilities of phase-change materials beyond the simple binary (2-state, amorphous or
crystalline) regime. Indeed, it has been suggested that these materials could provide a ‘cognitive’ data processing functionality in the optical and electrical regimes[2.25][2.26]. Being able to store information in the degree of disorder in the material could provide a route to higher-data density through higher-base memory[2.27]. To create this functionality, the material in question must demonstrate the ability to form either pre-threshold states, multi-level states, or both.

Pre-threshold states utilise an accumulative property of phase-change materials; successive identical pulses applied to an amorphous film will cause some structural ordering in the pre-threshold state, with little or no change in optical properties. This means that the material can accumulate inputs with little optical change, and then after an arbitrary number of pulses, switch to a dramatically different state with sharply contrasting optical properties. The ability for the material to ‘remember’ its excitation history without appearing to change, and then switch its properties at threshold with high contrast, could potentially be of great importance in optical data processing. The mechanism relies on some form of structural ordering which prepares the material for the threshold switching event.

The act of ordering the structure of the glass in these pre-threshold states is referred to as ‘pre-structural ordering’ or ‘priming’[2.28][2.29]. The pre-threshold excitations induce nucleation seeding, which results in the crystallisation process being much more rapid when it does finally occur; the nucleation has already been performed, so on the threshold switch, crystal formation is only limited by the growth rate of the crystal. Indeed, Loke et. al. have demonstrated that by incubating the phase-change layer, the crystallisation speed is much higher; ultrafast voltage-induced crystallisation in as little as 500 ps has been demonstrated[2.28]. The incubation is said to result in an ‘overall structural ordering with development of clusters in the amorphous matrix’, which facilitates a much faster crystallisation event when the system is given sufficient energy to do so.

Multi-level switching is similar conceptually, but here each successive identical optical pulse results in a progressive shift in the optical properties. The material’s optical properties can be gradually shifted from those in its fully amorphous state to those in its fully crystalline state, offering the storage of multiple bits per mark. This has already been demonstrated in the electrical regime[2.27]. This is of particular interest for ‘cognitive’ data processing applications[2.30], where the material acts as a processor as well as memory.

2.4 Conclusions

In this chapter, the structures of both GST and GLS glass have been investigated to explain their attractive attributes as phase-change materials, such as their high contrast
between crystalline and amorphous phases in the electrical and optical regimes. Both were successfully sputter-deposited as thin films, and laser crystallisation was attempted on both materials using a Labview-based CW crystallisation system which allowed parameters to be swept efficiently. GST films were successfully crystallised, and different crystalline fractions were identified in the resultant crystalline marks. However, GLS films were not successfully crystallised. Pre-threshold and multi-level switching in GST was then discussed in the context of offering multi-base memory or arithmetic processing by means of continuously altering the crystalline fraction in the film. This continuous tunability of crystallinity offers the desirable prospect of a tunable phase-change metamaterial resonance in a hybrid device.

References


REFERENCES


Chapter 3

Electromagnetic Metamaterials

3.1 Introduction to Plasmonics and Metamaterials

Surface plasmons are defined as quanta of charge density oscillations of the free electron gas at a metal-dielectric interface. The field of plasmonics, a discipline of nanophotonics, involves the interaction of electromagnetic radiation with metals on sub-wavelength length scales. The interaction of the incident electromagnetic field with the conduction electrons in metallic nanostructures can confine and enhance the radiation in the near-field, leading to intriguing optical effects[3.1]. At low frequencies, the free conduction electrons oscillate $\pi$ out of phase with the excitation field; this results in negative permittivity values and a high reflectivity. As the frequency of the driving electromagnetic field tends to the reciprocal of the characteristic relaxation time for the electrons in the metal, $\tau$, the phase relationship between the driving field and the induced currents changes. This is one reason for the strong frequency dependence in plasmonic nanostructures, which can be quantified by the complex dielectric function $\epsilon(\omega)$.

Metamaterials are an exciting new paradigm in photonics that concerns the interaction of light with materials patterned on the sub-wavelength scale, heavily exploiting surface plasmon resonances. They can be considered as the subwavelength surface plasmon analogy of photonic crystals, where the dielectric function of the material can be engineered through the geometry of nanoscale patterning of a plasmonic layer[3.1]. Although the first metamaterial is often attributed to Bose in 1898[3.2], these materials were largely inspired much later on by microwave frequency selective surfaces[3.3]. The potential scope of applications of these materials is vast, and many fascinating effects have already been discovered, such as negative-index media[3.4], surface plasmon lasing[3.5] and cloaking[3.6][3.7].
3.2 Metamaterial Theory

Photons couple strongly to free electrons in metals, and weakly to bound electrons in dielectrics. Metamaterials utilise the strongly contrasting nature of these two optical material types to define resonator geometries which are periodic on the subwavelength scale, and hence create materials with spectral dispersions not found in nature\[3.8\].

Typically, if the unit cell size of each resonator is $d$ and the wavelength of incident radiation is $\lambda$, then if the condition $d << \lambda$ is fulfilled (typically $d < \lambda/10$), the material can be described by the relative effective permittivity and permeability, $\epsilon$ and $\mu$. The scattering properties of objects structured on this length scale determine $\epsilon$ and $\mu$; not just simply the atoms they are composed of; therefore there is a requirement to define both terms as ‘effective’.

The incident electromagnetic wave induces oscillating currents in the metallic nanostructures, which then act as scattering sources (nanoantennas). Each complete unit cell of the nanostructures, typically including two asymmetric oscillator arms, can be defined as a meta-atom. How these antennas scatter determines the ‘response’ of the metamaterial. The nanostructures can be designed so as to display resonant behaviour at a certain frequency $\omega_R$, which causes the oscillating currents to be strongly coupled to the incident field, and hence amplified at that particular frequency. This results in a ‘strong’ response in the meta-atoms, producing, for example, a strong magnetic dipole moment.

The split-ring resonator (shown in Figure 3.1) has been widely studied in the metamaterial community. The design presents an inductance $L$ due to the metallic ring, and a capacitance $C$ due to the gap or ‘split’ in the ring. Hence the structure can be simplified as an $LC$ oscillator circuit, as shown in Figure 3.2.

The resonance condition for an $LC$-oscillator is given in Equation 3.1,

$$\omega_{LC} = \frac{1}{\sqrt{LC}},$$  \hspace{1cm} (3.1)

where $\omega_{LC}$ is the resonance frequency of the resonant element. In the infrared part of the spectrum, metals can still support conduction currents, so Equation 3.1 provides a good, if simplified, approximation. In the visible however, plasmons dominate, and different mathematical relationships and physical designs are required to obtain resonant behaviour.

The Asymmetric Split-Ring (ASR) metamaterial uses symmetry breaking as a result of the uneven arms in the structure to create ‘trapped modes’, as shown in Figure 3.3\[3.9\]. The trapped mode consists of the conduction currents and surface-plasmon-polaritons in the ASR arms oscillating in antiphase, where a surface-plasmon-polariton is defined as
Figure 3.1: A split-ring resonator in different orientations exciting different modes. The blue rings represent metal rings immersed in a dielectric medium. Ring A shows coupling to the $LC$ resonance via the electric field, which is possible at incidence normal to the plane of the ring. Ring B shows no coupling to the $LC$ resonance at normal incidence. Ring C displays coupling to the $LC$ resonance via the magnetic field component; however the plane of the resonators has to be parallel to the direction of propagation of the incident wave. The resonance can be excited given that the magnetic component is normal to the plane of the ring and the electric component is normal to the cut side of the resonator.

Figure 3.2: A simplified $LC$ circuit model of a split-ring resonator.
Chapter 3 Electromagnetic Metamaterials

Figure 3.3: A classical analogue of Electromagnetically Induced Transparency (EIT) utilising resonant modes in a metamaterial. The symmetrically split ring displays an absorption resonance at the resonance frequency, $\nu_R$. This is due to a symmetric electric dipole resonance mode, which is shown as a trough in the transmission spectrum. Breaking the symmetry of the resonator as in the case of the asymmetric split-ring creates an antiphase oscillation at $\nu_R$. This trapped-mode resonance in the asymmetrically split ring results in a transmission peak in the spectrum; the asymmetry induces transparency in the metamaterial[3.13][3.14].

A quasiparticle formed as a result of the coupling between an oscillating surface charge density and an incident electromagnetic wave at a metal-dielectric interface[3.10]. This ‘Fano’ resonance is a result of the interference between a discrete narrow resonance and a continuum, and results in a steep dispersion[3.11]. The frequency-dependence of this trapped mode is expanded on in Figure 3.4. This narrow lineshape lends itself particularly well to high-contrast, sensitive optical devices, as the nature and position of the resonance is influenced strongly by its dielectric environment[3.12]. Measuring reflection and transmission spectra therefore provides an ‘amplified’ method of measuring small changes in the local refractive index. The nature and position of the resonant features in the reflection and transmission spectra can be engineered via tailoring the unit cell design of the metamaterial.

Weak coupling to free space afforded by the trapped mode results in long lifetimes in
Figure 3.4: The trapped mode in an asymmetric split-ring resonator, where $\nu_1 < \nu_2 < \nu_3$. In A, with the incident field oscillating at a frequency $\nu_1$, the longer arm of the resonator is resonant. There is a net electric dipole induced in the resonator in the direction of the electric field excitation, and the system has high losses. In B, driven at $\nu_3$, the shorter arm is resonant, and again the system is lossy. In C however, the induced currents in both arms are of similar magnitude, and the net induced electric dipole moment nearly cancels. This results in a high-$Q$ resonance called a ‘trapped’ mode, which has minimal radiative losses (minimal coupling to free space). This eigenmode with an oscillating circular current flow produces a corresponding oscillating magnetic moment perpendicular to the plane of the resonator.
Chapter 3 Electromagnetic Metamaterials

Figure 3.5: Symmetric and antisymmetric modes in ASRs; the red arrows show the directions of propagation of the scattered radiation, described by the propagation vector $k$. The symmetric mode scatters strongly in the forward and backward directions due to the net electric dipole mode. This is an electric resonance. The antisymmetric mode supports an oscillating circulating current mode, which generates a magnetic dipole perpendicular to the plane of the resonator, and thus causes the radiation to be trapped in the plane of resonator. This is a magnetic resonance. The scattered electromagnetic radiation out of the plane is weak; the electric and magnetic dipole radiation components propagating out of the plane cancel due to destructive interference[3.15].

The resonators, which create narrow spectral lines. The $Q$-factor is given by $Q = \nu_0/\Delta \nu$, where $\nu_0$ is the frequency of the peak in transmission, and $\Delta \nu$ is the bandwidth of the region greater than half of the transmission maximum. This $Q$-factor decreases as the asymmetry of the split ring is increased. Therefore attaining the highest $Q$-factor is a compromise between creating a strong trapped mode through asymmetry to minimise radiative losses, whilst maintaining resonator symmetry. Reducing losses in the resonator also increases the $Q$-factor.

The antisymmetric case in Figure 3.5 provides coupling to other resonators via magneto-inductive waves; this makes the array of resonators coherent. A highly-ordered pattern of resonators results in the highest quality factor in coherent metamaterials; the resonance becomes collective. Further, a single ASR exhibiting its trapped mode shows strong scattering, but in a perfect infinite two-dimensional array of ASRs there is no scattering. As another way of defining $Q$-factor is $Q = \text{stored energy/scattered energy}$, it can be seen that a larger array of resonators produces a higher $Q$-factor. The resultant array is a periodic scattering interface, which is sufficiently sub-wavelength as to display minimal diffraction.

In summary, a large two-dimensional array of asymmetric split-ring resonators can exhibit a collective trapped-mode resonance, which results in sharp spectral features. The position of these resonant features can be determined via unit cell design. Small changes
in the local dielectric environment of the resonators can result in a significant modification of the reflection and transmission spectra.

3.3 Metamaterial Fabrication and Characterisation

3.3.1 Focussed Ion Beam

In order to fabricate metamaterial structures, it is necessary to deposit a thin film of gold, typically 50 nm, onto a substrate via electron-beam evaporation, which is then patterned with the required metamaterial design. 50 nm of gold was chosen as this is approximately the penetration depth of the electromagnetic wave associated with the surface-plasmon-polariton in the visible to near-infrared wavelength range. Therefore choosing this thickness of gold supports excitation of surface-plasmon-polariton modes in the metamaterial over this wavelength range[3.16].

The Dual Beam FEI Helios 600 Nanolab Focussed Ion Beam (FIB) is a dual-beam SEM and FIB system which allows milling on the nanoscale using Ga\textsuperscript{+} ions to ‘sputter out’ regions of material. This allows rapidly reconfigurable patterning of metamaterial structures in thin films over small areas, and is the main method for generating metamaterials down to 25 nm linewidth. Regions of gold thin film can be milled away to leave metallic resonators (in the case of a positive metamaterial). However, this method is time-intensive and in practice results in poor-quality milling, which is reflected in low quality-factor resonances.

However, Babinet’s principle can be applied such that if a metal (positive) structure is the source of an electric field, the inverse (negative) structure is the source of a magnetic field. Therefore the inverse, or negative, ASR pattern will have a complementary resonance spectrum to the positive one, with the advantage that the structure is far easier to fabricate via FIB; the arms of the resonator are milled out of a gold film. The design of the resonator can also be simplified for nanofabrication; the loss in quality factor due to deviation from the original design is compensated for by fewer fabrication errors in the simplified version. A single negative ASR is shown in Figure 3.6.

A 10×10 ASR array is shown in Figure 3.7, and the effect of various ion milling dosages are explored in Figure 3.8. A full metamaterial array of sufficient size to be experimentally characterised is shown in Figure 3.9, which required approximately 20 minutes to mill.

The FIB-fabricated patterns may deviate from the ideal ASR pattern through inhomogeneities between unit cells (edges are rounded, asymmetric ‘arms’ etc.). This is largely attributed to errors in the focus and astigmatism correction of the ion beam, or use of a non-optimal beam current. Gallium ion contamination from FIB can increase
Figure 3.6: A single ASR, milled in a 50 nm gold thin film, with a unit cell size of 400 nm, and a linewidth of approximately 35 nm, milled using a line dosage of 25 nC cm$^{-1}$. The sides of the FIB cut are slightly bevelled; the width of the top cut is slightly wider than the bottom.

Figure 3.7: An SEM image of ASRs fabricated by FIB in a 50 nm gold layer. The unit cell size is 400 nm, and the thickness of the gold layer is 50 nm. The milling line dosage was 25 nC cm$^{-1}$.
Figure 3.8: 4 ASR arrays milled with different ion dosages. In the order top-left, top-right, bottom-left, bottom-right, the ion doses were 15, 20, 25 and 30 nC cm$^{-1}$. Underexposure results in milling errors (incomplete rings, irregular patterning), whereas overexposure results in an excessive linewidth which deviates from the original resonator design. In this case, the optimal dosage was determined to be 25 nC cm$^{-1}$, in the bottom-left of the figure.

Figure 3.9: An ASR array, $31 \times 31 \mu m$ in size, which is large enough to obtain an experimental reflection/transmission spectrum, milled using a line dosage of 25 nC cm$^{-1}$. The dosage test pattern is visible in the bottom of the image, and the bright object in the bottom-right is a flake of gold film created by a scratch on the surface, used for locating the metamaterial region during optical characterisation.
absorption, and surface roughness can add to scattering losses. These factors all detrimentally affect the quality factor of the obtained resonance; they dampen the resonance features[3.15].

3.3.2 Microspectrophotometer

The CRAIC UV-vis-NIR Microspectrophotometer is a spectrometer arranged in a microscope configuration, and can acquire both transmission and reflection spectra from regions on the micron scale, over the wavelength range 400-2100 nm. The tool is vital for experimentally characterising the optical response of metamaterials, where even regions on the micron length scale are difficult and time-intensive to produce. The incident light can be polarised in any desired direction. The metamaterial array shown in Figure 3.9, composed of ASR unit cells shown in Figure 3.6, produced the spectrum shown in Figure 3.10.

Figure 3.10: The trapped mode is characterised by a peak in absorption (A) (here around 1.525 µm), and steep gradients in both reflection (R) and transmission (T) spectra.
3.4 Phase-Change Metamaterials

3.4.1 Concept of PCMMs

Phase-change metamaterials consist of a thin film of phase-change material in close proximity to a subwavelength periodically structured plasmonic thin film (metamaterial). The metamaterial provides a sharp ‘Fano’ resonance in the spectrum. Switching the phase-change layer from amorphous to crystalline results in an alteration of the dielectric environment adjacent to the metamaterial, and produces a corresponding change in the resonance wavelength. This alters the transmission and reflection characteristics of the hybrid structure; the most obvious response is a shift in wavelength.

Switching the phase-change layer provides a means of modulating the metamaterial’s optical properties, and it may offer progressive, rapid tunability. The non-volatility of phase-change materials can also enable a memory effect, where the optical state of the chalcogenide and therefore the metamaterial will remain unchanged until the next switching event. Combining a switching and memory functionality with the unique properties of metamaterials could lead to new applications in active optical devices.

3.4.2 Prior Art

Phase-change metamaterials with chalcogenides have not been extensively studied. Attempts at creating a memory metamaterial using a transition metal oxide and the principle of memory-capacitance have only demonstrated a 10 minute information retention[3.17]. Frequency-tunable PCMs using vanadium oxide can offer a 100 nm resonance shift on impressively fast timescales, but has no memory functionality[3.18]. Impressive transmission changes of up to 50% have been reported in temperature-driven reconfigurable photonic metamaterials, but again no memory functionality is present[3.19].

Chalcogenides have already been proven to be effective active plasmonic modulators[3.20]. Here, a silver layer on a GLS layer offers plasmonic modulation through reversible photo-induced changes in the chalcogenide. A chalcogenide PCM electro-optic switch was created by Sámon et. al., using GLS glass. This device produced a 150 nm resonance shift in the near-infrared with a 4:1 transmission modulation contrast ratio, using an electrical phase-switching mechanism[3.21]. All-optical modulation in a similar device using GST was realised by Gholipour et. al.[3.22].

Different metamaterial structures using chalcogenides have also been used recently to create similar resonance shifts; for example, using infrared nano-antennas[3.23] and elliptical nanohole arrays[3.24]. However, a progressive resonance shift with memory and logic functionality has not yet been demonstrated. Furthermore, little work has been done concerning femtosecond switching of chalcogenide thin films in such structures.
3.4.3 Fabrication Steps

The device was developed as follows. The ZnS-SiO$_2$ buffer and capping layers were necessary to prevent the GST from reacting with either the oxygen in the atmosphere or the gold film.

1. A substrate was selected based on the optical characterisation required of the finished device (optimal for NIR, MIR etc.) (borosilicate glass, microscope coverslip, CaF$_2$ or fused quartz)

2. A gold film of 50 nm was deposited by e-beam evaporation. The base pressure was allowed to reach $5.00 \times 10^{-6}$ Torr before the deposition, and the beam current continually adjusted to maintain a deposition rate of 0.2 Å s$^{-1}$

3. The gold film was patterned with ASRs via FIB milling using a line dosage of 25 nC cm$^{-1}$

4. A buffer layer of 50 nm ZnS-SiO$_2$ was sputtered using a base pressure of $9.00 \times 10^{-5}$ Torr or lower, an argon flow rate of 35 cc min$^{-1}$ and a gun forward power of 70 W

5. The phase-change layer of 50 nm (GST, for example) was sputtered using a base pressure of $9.00 \times 10^{-5}$ Torr or lower, an argon flow rate of 35 cc min$^{-1}$ and a gun forward power of 35 W

6. The final capping layer of 50 nm ZnS-SiO$_2$ was sputtered to prevent oxidation of the phase-change material, using identical parameters to the previous ZnS-SiO$_2$ step.

3.4.4 Experimental Characterisation

The phase-change metamaterial devices were then crystallised in two separate ways, using both a hot plate and successive femtosecond pulses, to attempt to manipulate the metamaterial resonance by altering the crystalline fraction in the phase-change material. The hot plate guaranteed crystallisation with minimal damage to the overall device structure, and was used as a standard to judge the femtosecond-induced crystallisation process against. The results of both regimes are shown and discussed in Chapter 6, in Figures 6.7-6.10.

3.5 Conclusions

Sub-wavelength structuring of materials to create periodic resonators produces metamaterials, which can have optical properties not found in conventional materials. Through
design of the resonator geometry and choice of materials used, dispersions can be tailored to a given application. One resonator design of interest is the ASR, as the asymmetry in the unit cell results in the trapped mode resonance which offers a sharp dispersion around the resonance wavelength. ASR metamaterial structures were fabricated by FIB milling, characterised using a microspectrophotometer, and the resonant features in the resulting spectrum were identified.

The trapped mode resonance in the ASR metamaterial is sensitive to its local dielectric environment; therefore altering the phase of an adjacent phase-change layer (and hence varying its refractive index) can tune the shape and spectral position of the resonance feature of the metamaterial. This could offer a non-volatile and non-mechanical platform to facilitate resonance tunability in a variety of metamaterial designs.

References


September 2010, Optoelectronics Research Centre, University of Southampton, 2011.


Chapter 4

Spectroscopic Ellipsometry

4.1 Introduction

Spectroscopic Ellipsometry (SE) is a non-destructive optical technique which uses the change in polarisation state on reflection from the sample of an incident polarised beam to deduce a wide range of information about the sample. The technique is applicable to a wide range of sample types, from bulk materials through to complex multi-layer thin film stacks. The complex dielectric function of a thin film can be obtained accurately, which acts as a ‘fingerprint’ for the material, whilst simultaneously providing information about the layer thickness and roughness. The technique is widely used in the semiconductor and optical coating industries\[4.1\].

In this instance, the technique provides a means of analysing how the dielectric function of the phase-change material changes after application of a heating laser pulse. The crystalline fraction of the glass (or equivalently the degree of order) will affect the dielectric properties of the layer, which in turn affects the metamaterial resonance response in the hybrid device. Accurate data for the dielectric function of the chalcogenide film is crucial for accurate modelling of the hybrid device, which will be elucidated in Chapter 5. This allows for a greater insight into the switching response of the device.

4.2 Theory

The basic premise of ellipsometry is that when incident light is reflected from a sample, its polarisation state is altered in some way. Light can be described as elliptically polarised when perpendicular polarisation components of the electric field are both of different amplitude and phase. This state of polarisation is frequently produced when linearly polarised light is reflected from a surface. Through measuring the change in phase and relative amplitude of perpendicular polarisation components on reflection,
certain information can be extracted from the sample. In the case of a bulk dielectric, for example a standard borosilicate microscope slide, the result is easily calculated from the Fresnel equations [4.2]. However, the calculation rapidly becomes much more complex in the case of multiple thin film layers on a transparent substrate, which is common in thin film research. In such a case, large numbers of variables are present, and the solutions become degenerate.

Ellipsometric modelling involves acquiring the ellipsometric angles $\Psi$ and $\Delta$ (defined in Equations 4.4 and 4.5) experimentally, then creating a model of the sample. The model then has $\Psi$ and $\Delta$ calculated for it for the spectral range required, and then the calculated data is fitted to the experimental data, via adjusting the parameters made available for fitting. Finally, the uniqueness and physicality of the fit is assessed to ensure the real values for the sample have been reported.

Ellipsometric analysis is the process of converting ellipsometric angles $\Psi$ and $\Delta$ into optical and physical properties of the sample being measured. The model takes into account the various layers and dispersions in the film stack, along with preliminary values for the fit parameters. The fitting algorithm performed by the software is of the Levenberg-Marquardt type; its aim is to minimise the Mean-Square Error (MSE) of the fit to the data through varying the parameters available to fit. Once a unique minimum MSE has been found, the parameters used to produce it are reported, thus finally providing optical and physical information about the sample. These parameters can then be put back into dispersion formulae to provide dielectric functions for the materials in the sample. Therefore whilst it is an indirect measurement technique, ellipsometry offers high-precision measurements of multiple variables, both optical and physical, simultaneously, making it an indispensable technique.

Spectroscopic ellipsometric data is represented by two variables, the ellipsometric angles $\Psi$ and $\Delta$, over a wavelength range, which are calculated from measured variables. Light polarisation can be described by $E_s$ and $E_p$, the electric field vectors perpendicular and parallel to the plane of incidence respectively. These can be used to describe the modification of polarisation by the complex Fresnel reflection coefficients, $r_p$ (polarised perpendicular to the plane of incidence) and $r_p$ (polarised parallel to the plane of incidence), as shown in Equations 4.1 and 4.2.

The complex Fresnel coefficients are given by

$$r_p = \frac{E'_p}{E'_p} = |r_p| \exp(i\delta_p),$$  \hspace{1cm} (4.1)

$$r_s = \frac{E'_s}{E'_s} = |r_s| \exp(i\delta_s),$$  \hspace{1cm} (4.2)
where $E_r$ and $E_i$ are the reflected and incident electric field vectors respectively. $|r|$ represents the ratio of the reflected and incident amplitudes, whilst $\delta$ is the phase change on reflection for that particular component.

The fundamental ellipsometric equation can now be defined as

$$
\rho = \frac{r_p}{r_s} = \tan(\Psi) \exp(i\Delta),
$$

(4.3)

where

$$
\tan(\Psi) = \frac{|r_p|}{|r_s|}, \quad 0^\circ \leq \Psi \leq 90^\circ,
$$

(4.4)

and

$$
\Delta = \delta_p - \delta_s, \quad 0^\circ \leq \Delta \leq 360^\circ,
$$

(4.5)

where $\rho$ is defined as the ratio of the perpendicular complex Fresnel reflection coefficients. $\Psi$ contains information about the ratio of the ratios of incident and reflected amplitudes for the $s$ and $p$ polarisation components. $\Delta$ is the difference between the phase changes for the $s$ and $p$ polarisation components. Through measuring the changes in amplitude and phase on reflection for $s$ and $p$ polarisation components, using the electric field vector and Equations 4.1 and 4.2, the complex Fresnel reflection coefficients for the sample can be calculated. Then using Equations 4.3, 4.4 and 4.5, the ellipsometric angles $\Psi$ and $\Delta$ can be calculated over a given wavelength range. These two variables contain all the necessary information for the fitting process, and thus allow indirect measurement of sample parameters.

The spectroscopic ellipsometer used was a Horiba Scientific Uvisel 2, which is a phase-modulated model with a spectral range of 190-2100 nm, achievable through the combined use of a photomultiplier tube and an InGaAs detector.

4.2.1 The Tauc-Lorentz Dispersion Formula

In order to be able to extract the dielectric function for GST, a suitable dispersion formula needs to be found. Once placed in the model, the model’s calculated $\Psi/\Delta$ data should approximately describe the features of the $\Psi/\Delta$ data obtained experimentally. The parameters of the dispersion formula for the GST can then be adjusted to provide the best possible fit to the experimental $\Psi/\Delta$ data, and these parameters are then used to calculate the complex dielectric function for the material.

The Tauc-Lorentz dispersion can be used to describe the optical functions of amorphous semiconductors accurately, and it has been used to ellipsometrically fit GST successfully in both the amorphous and crystalline states[4.3][4.4]. The real and imaginary parts of the complex dielectric function are given by
\[
\epsilon_1(E) = \epsilon_{\infty} + \frac{2}{\pi} \cdot P \int_{E_g}^{\infty} \frac{\xi \epsilon_2(\xi)}{\xi^2 - E^2} \, d\xi, 
\]
(4.6)

\[
\epsilon_2(E) = 2n(E)k(E) = \begin{cases} 
\frac{1}{E} \cdot \frac{AE_0 C(E-E_g)^2}{(E^2-E_0^2)^2+C^2E^2}, & E > E_g \\
0, & E < E_g 
\end{cases}, 
\]
(4.7)

where

- \(\epsilon_1\) = real part of the complex dielectric function,
- \(E\) = photon energy,
- \(\epsilon_{\infty}\) = high frequency dielectric constant,
- \(P\) = Cauchy principal value,
- \(E_g\) = band gap,
- \(\xi\) = frequency being integrated over,
- \(\epsilon_2\) = imaginary part of the complex dielectric function,
- \(A\) = amplitude of absorption peak,
- \(E_0\) = peak in the joint density of states,
- \(C\) = broadening factor.

The Tauc-Lorentz dispersion given in equations 4.6 and 4.7 was found to offer the best fit to the data for GST films, the results of which are presented in the following sections.

### 4.2.2 Variable Angle Spectroscopic Ellipsometry

Variable Angle Spectroscopic Ellipsometry (VASE) is a technique commonly used when studying thin films on transparent substrates. The ellipsometric data is acquired at a variety of angles, rather than just one, and the model parameters are simultaneously fitted to the data over all angles. The result is not only a lower error in the derived values, but also a reduced possibility of the fitting procedure becoming ‘stuck’ in a local minimum. This problem of local minima preventing discovery of the true global minimum by the fitting algorithm is particularly prevalent with thin, highly transparent films on transparent substrates. As the only disadvantage of the VASE method is increased duration of data acquisition and modelling time, the technique was applied in the case of GST. Figures 4.1 and 4.2 demonstrate the fitting at multiple angles.
Figure 4.1: $\Psi/\Delta$ plot for an amorphous 100 nm GST film on a microscope coverslip, with no capping layer, at different angles of incidence, simultaneously fitted to the same model.

Figure 4.2: $\Psi/\Delta$ plot for a crystalline 100 nm GST film on a microscope coverslip, with no capping layer, at different angles of incidence, simultaneously fitted to the same model.
4.3 Results

4.3.1 Amorphous and Crystalline GST Thin Films

The technique was applied to 100 nm thin films of GST deposited on borosilicate microscope cover slips from Agar Scientific, at an incidence angle of 70°. The results for the amorphous and crystalline cases are shown in Figures 4.3 and 4.4 respectively.

![Figure 4.3: Ψ/∆ plot for an amorphous 100 nm GST film, uncapped, on a microscope coverslip.](image)

The model used included a coverslip substrate (whose dispersion was determined via ellipsometry prior to the combined model), a 100 nm GST layer using a Tauc-Lorentz dispersion (with starting parameters from [4.4]), and a 10 nm roughness layer. This model provided a good fit with realistic parameter values, giving a $\chi^2$ of 1.82 and 0.20 for the amorphous and crystalline cases respectively. As the two fits are acceptable, the derived dispersion for the GST layer in Figure 4.5 is of physical significance.

However, the dispersion of Figure 4.5 did not agree with other literature, and there was little contrast between the amorphous and crystalline states; at $\lambda = 1200$ nm, Nemec et. al. give values of $n = 4.65$, $k = 0.40$ in the amorphous state and $n = 6.60$, $k = 1.90$ in the crystalline state[4.4][4.5]. This discrepancy is consistent with the uncapped chalcogenide layer being partially oxidised by the atmosphere, resulting in a lower real part of the refractive index in both the amorphous and crystalline states, and less contrast between them. Therefore a protective ‘capping’ layer was added to protect the GST
Figure 4.4: Ψ/Δ plot for a crystalline 100 nm GST film, uncapped, on a microscope coverslip.

Figure 4.5: n/k plot for 100 nm GST, uncapped.
from oxidation; the results of ellipsometry on the non-oxidised GST film are given in Figure 4.7.

### 4.3.2 ZnS-SiO$_2$

Traditionally in phase-change media, ZnS-SiO$_2$ has been used to provide a closely index-matched inert layer to prevent the GST reacting with neighbouring materials whilst maintaining high optical contrast in an optical storage situation\[4.6\]. As the dispersion of this material varies strongly with its composition, it was important to acquire an accurate dispersion for the exact material being deposited, which can vary from the initial sputtering target composition\[4.7\]. 50 nm ZnS-SiO$_2$ in the compositional ratio 80:20 was sputtered onto a microscope coverslip, then measured and modelled on the ellipsometer to produce Figure 4.6.

![Figure 4.6: n/k plot for ZnS-SiO$_2$. The value of k was negligible, and was set to zero by the fit.](image)

### 4.3.3 Capped GST

A 30 nm GST layer was sandwiched between two 10 nm ZnS-SiO$_2$ layers on a coverslip substrate, to provide the GST with an inert environment to change phase; this allows extraction of the dispersion of pure amorphous and crystalline GST through modelling.
The extracted dispersions for amorphous and crystalline GST shown in Figure 4.7 are in good agreement with literature[4.4]. The material demonstrates high refractive index contrast between its two phases for wavelengths from 1 µm to 2.1 µm. Over the same wavelength range, the extinction coefficient provides considerable contrast between the two phases.

It is well known that the two phases of GST are optically high-contrast, and this has historically been used to great advantage in the optical storage community[4.8]. Knowing the precise dispersions of the material’s phases allows for accurate modelling of the hybrid metamaterial device’s response as a result of a change of phase in the chalcogenide layer.

4.3.4 Au

Finally, the gold deposited by e-beam evaporation was measured and fitted using a Drude model with a high-frequency permittivity modification[4.9], which is used to take account of interband transitions, given by

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + \Gamma^2} + i \frac{\omega_p^2\Gamma}{\omega(\omega^2 + \Gamma^2)}.$$  \[4.8\]
where

\[ \varepsilon_\infty = \text{high-frequency permittivity,} \]
\[ \omega = \text{photon frequency,} \]
\[ \omega_p = \text{plasma frequency,} \]
\[ \Gamma = \text{damping constant.} \]

The result of the fit using Equation 4.8 is presented in Figure 4.8. The data is in reasonable agreement with the literature, although there are some differences, especially at longer wavelengths, as seen in Figure 4.9[4.10][4.11]. The values of \( \varepsilon_1 \) and \( \varepsilon_2 \) were within 22.0% and 27.3% of Palik’s data values respectively, although deposition method and conditions can affect the dispersion of gold films significantly. Having the exact dispersion for the gold that is deposited in the final device is important for accurate modelling, as will be shown in Chapter 5.

![Dielectric function of gold](image)

Figure 4.8: Dielectric function of gold, extracted from ellipsometry measurements.
4.4 Conclusions

Spectroscopic ellipsometry was used to determine the dispersions of all of the materials used in the phase-change metamaterial device, with the aim of increasing modelling accuracy to better represent experimental results. After the inclusion of a ZnS-SiO$_2$ capping layer to prevent oxidation of the GST films, variable-angle spectroscopic ellipsometry modelling using a Tauc-Lorentz dispersion formula accurately described the dispersion of a thin film of GST in both amorphous and crystalline phases, in good agreement with the literature. The dispersion of gold thin films was also extracted for the specific films deposited in house, which were found to differ from the literature values. The extracted dispersions for all materials were then used in the modelling process to ensure the highest accuracy possible in the resulting simulated spectra.

References


Chapter 5

Modelling

5.1 Introduction

Modelling is a vital component of metamaterial research in the optical regime chiefly because of the time and cost associated with fabrication. Using a technique such as FIB milling on a sample requires lengthy calibration and alignment steps, and milling a region large enough to be probed optically (typically around 900µm²) can take a significant amount of time.

Using a Finite Element Modelling (FEM) package such as COMSOL Multiphysics 4.3 for electromagnetic numerical simulations allows an environment to be created where physical parameters can be varied and optical responses checked far more rapidly than would be possible with a conventional fabricate and test approach. It also helps remove error due to fabrication variations and problems from batch to batch. An additional advantage of modelling is that it offers a greater understanding of the response of a metamaterial unit cell through visualisation of the conduction and displacement currents and electric and magnetic fields.

5.2 The Modelling Environment

Finite element modelling for electromagnetic frequency-domain problems consists of breaking the problem down (meshing) into three-dimensional elements, commonly tetrahedrons, and solving Maxwell’s equations in three dimensions over those elements for a variable such as electric field.

In Figure 5.1, the scattering boundary conditions determine the electric field at the top (incident) and bottom (transmission) boundaries. The sides of the bounding box (in the z-x and z-y planes) are perfect electric conductors, and the model employs periodic
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Figure 5.1: A typical model for a negative metamolecule in a gold layer on a substrate. The negative ASR unit cell is 400 nm × 400 nm in the x-y plane, milled into a 50 nm Au layer. The model extends 1 μm above and below the plane of the resonator in the z-direction. A y-polarised plane wave is set to propagate vertically downwards from the top boundary of the model, in order to enable excitation of the trapped mode.

boundary conditions in the x- and y-directions to create an array. A two-dimensional mesh with triangular elements was created on the bottom surface of the gold layer. The maximum mesh element size was never allowed to exceed λ/(10n) (where n is the refractive index in that particular medium) in this plane, to ensure sufficient mesh resolution to describe the electromagnetic field in high fidelity in this crucial area. The triangular mesh was then swept up through the thickness of the gold layer (and ‘cut-out’ air resonator) using the same maximum element size condition. The mesh was then allowed to grow in three-dimensional tetrahedrons from the top and bottom faces of the gold layer up to λ/(10n) in the surrounding air, which could afford to have a far coarser mesh. Using this method, models with around 6 × 10^4 elements were successfully solved
A COMSOL server was established on the University of Southampton’s Iridis High Performance Computing Facility (on multiple nodes to ensure enough RAM was available for the computation, typically 4 nodes with 24 GB RAM and 12 cores each) and was controlled via a MATLAB script, which passed values to COMSOL to enable parameter sweeping. The script passed a given wavelength to COMSOL, along with the permittivities for the materials at that wavelength, which were interpolated from the ellipsometry data. In this way a wavelength sweep could be performed in the model, with the material permittivities varying as determined experimentally. Solution times for a $6 	imes 10^4$ element model were around 6 minutes per wavelength.

5.3 Modelling Results

5.3.1 Negative ASRs in Gold

The simulated reflection, transmission and absorption spectra for a 400 nm unit cell negative ASR in a 50 nm Au film on a quartz substrate is shown in Figure 5.2. The experimental result of the same design is given in Figure 5.3, and the $Q$-factor calculated by dividing the transmission maximum frequency (at 1.62 µm in the experimental case) by the half-maximum bandwidth. The trapped mode resonance has a lower quality factor than the modelled case; the most likely cause of this is fabrication imperfections, deviating from the ideal ASR design.

5.3.2 Phase-Change Metamaterial

The full phase-change metamaterial device was then modelled; a 10 nm ZnS/SiO$_2$ layer and then a 30 nm GST layer were added on top of the 50 nm Au layer in Figure 5.2. The dielectric functions of both amorphous and crystalline GST (obtained via ellipsometry) could then be included in the model to assess the nature of the resonance for each phase of the GST. In the previous case, the triangular mesh which was swept through the thickness of the gold layer was now extended to sweep upwards through both the ZnS/SiO$_2$ and GST layers. The mesh was allowed to grow as before from the top GST surface and the bottom gold surface into the air. Again using the maximum element side length condition of $\lambda/(10n)$, this brought the total number of elements in the model up to approximately $1 \times 10^5$.

Figures 5.4, 5.5 and 5.6 show the modelled evolution of the spectra for the phase-change metamaterial as the GST is crystallised. A half-crystalline intermediate state of the GST was created by averaging the amorphous and crystalline dispersions obtained ellipsometrically.
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Figure 5.2: The trapped mode is located at 1.75 µm, and the reflection and transmission spectra in this region are steep. Shifting the resonance by a small amount would result in a significant change in reflection or transmission if the device was probed at the resonance wavelength.

Figure 5.4, the amorphous case, shows pronounced resonance features. As the phase-change layer becomes more crystalline through Figures 5.5 and 5.6, the resonance features become less well-defined and appear to be red-shifted to longer wavelengths. Although the trapped-mode resonance appeared to be outside the 1-2 µm range of the model, the other resonance mode visible in the reflection and transmission spectra clearly shows a significant red-shift in position and reduction in quality factor due to the crystallisation of the chalcogenide layer, in qualitative agreement with similar work[5.1][5.2][5.3].

Previous experimental work characterising an identical structure to the one in these models had shown a weak trapped-mode resonance in the amorphous case at approximately 1.5 µm, hence the reason for modelling this structure over the wavelength range 1-2 µm.

5.3.3 All-Dielectric Metamaterial

Recent work has shown that it is possible to demonstrate a near-infrared trapped-mode magnetic resonance in an all-dielectric structure[5.4]. Using two dissimilar silicon nanobars in each unit cell, Zhang et al. were able to demonstrate experimentally a Q-factor
Figure 5.3: The trapped mode is exhibited experimentally at 1.525 µm, 225 nm less than in the modelled case. The absorption resonance is broader than in the modelled case, and the contrast between the peaks and troughs of the reflection and transmission spectra is significantly less. This is ascribed to the deviation of the milled structure from the modelled design, and surface roughness in the gold film causing scattering.

of 15, although this was believed to be largely limited by fabrication difficulties, as the modelled Q-factors were significantly higher. In plasmonic metal nanostructures, Joule losses due to the induced conduction currents are a significant limitation in the maximum obtainable Q-factor; the material itself causes losses, even with perfect fabrication. In the all-dielectric case however, the oscillating displacement currents are near-lossless, although the interaction is much weaker.

The hybrid phase-change metamaterial structure, with plasmonic gold layer and switchable chalcogenide layer, does not offer drastic resonance modulation on switching. This is mainly due to the separation of the two components; the resonant metamaterial layer is itself unchanged, only its dielectric environment is altered through switching of the adjacent GST layer. Detrimentally, the GST has to be separated further by a buffer layer to prevent chemical degradation of the chalcogenide. This results in a smaller resonance modulation with increasing separation between the two layers.

In light of the all-dielectric work with silicon, GST could be a potential candidate for a switchable all-dielectric metamaterial. The amorphous, dielectric phase would be quasi-lossless, much like silicon, with oscillating displacement currents. After switching, the
Figure 5.4: The trapped mode is not obvious in the absorption spectrum. However, the reflection and transmission spectra indicate that the resonance potentially lies at a wavelength longer than the limit of the axis; the absorption begins to increase around 2.0 µm. The peak in transmission and trough in reflection around 1.45 µm are ascribed to modes other than the trapped mode.

crystalline phase would behave far more conductively, with more significant Joule losses due to the presence of conduction currents. It was hypothesised that due to the chalcogenide simultaneously behaving as the resonator and switching medium, and the device being able to switch from being quasi-lossless to lossy, this might offer more significant modulation of the resonance, leading to a more high-contrast switchable metamaterial device.

Additionally, GST is a good material candidate for dielectric metamaterials as its high refractive index ensures that the resonators are suitably sub-wavelength to minimise diffraction. Additionally, the low absorption (at least in the amorphous state) minimises losses in the resonators.[5.4]

Using the dissimilar nano-bar structure of Zhang et. al. with positive GST bars, shown in Figure 5.7, the amorphous and crystalline cases were simulated in Figures 5.8 and 5.9 respectively. To excite the trapped mode, the incident radiation was polarised with the \( E \)-field parallel to the long axis of the bars.

Fabrication of the structure would not be without difficulty due to charging of the amorphous chalcogenide during milling resulting in a poorly-defined linewidth and therefore some deviation from the original design, which would reduce the quality factor. Also the...
Figure 5.5: The resonance features appear to have red-shifted. The peak in transmission and trough in reflection in Figure 5.4 have both moved to 1.75 µm, indicating that the trapped mode must also have shifted to a longer wavelength. The quality factor of the feature at 1.75 µm is substantially reduced, and the absorption across the wavelength range is increased.

GST would need to be protected from the atmosphere at all times to prevent oxidation, which may be difficult after the structure has been milled.

It would be beneficial to model the crystalline nanobars at longer wavelengths, to attempt to locate the exact position of the shifted trapped mode. Nevertheless, this model indicates that a trapped mode resonance could be supported in a GST all-dielectric metamaterial, and that the sharp spectral features associated with it could be radically altered through crystallisation of the chalcogenide. This system therefore has potential as an all-dielectric non-volatile tunable metamaterial.
Figure 5.6: The peak in transmission and the trough in reflection are now deeply red-shifted to 1.925 µm, and it is assumed that the trapped mode has again shifted to a still longer wavelength. The quality factor of the resonant features is now low, and the absorption of the device over the displayed wavelength range is significant.
Figure 5.7: The all-dielectric metamaterial model, which is similar in construction to the negative ASR model in Figure 5.1. The two nanobars are positive; they are assigned the complex dielectric function of GST and are of slightly different lengths to break the symmetry in the unit cell. The unit cell is 900×900 nm, the bars are 300 nm wide, 160 nm thick; the short bar is 650 nm long and the long bar is 750 nm long.
Figure 5.8: The modelled spectra produced by the dielectric metamaterial structure in Figure 5.7, with the bars in the amorphous state. The trapped mode appears to be at 1.675 µm, and is sharp and well-defined.
Figure 5.9: On switching to the crystalline state, the spectrum is radically altered; the absorption is much higher across the wavelength range as would be expected. The trapped mode which was originally obvious at 1.675 µm is no longer present in the spectrum. In line with previous simulations, it is thought that the trapped mode has been both red-shifted outside of the modelled wavelength range and broadened.
5.4 Conclusions

The main motivation for modelling the response of the phase-change metamaterial devices was the time and associated cost of fabricating and characterising the device. Using ellipsometrically-obtained values for the dispersions for all of the materials used, the model of the negative ASR in isolation showed a similar structure in the modelled reflection, transmission and absorption spectra to the experimentally-realised device. The $Q$-factor of the model was higher than in the experimental data, as would be expected, but the resonance features in the model were red-shifted by 225 nm relative to the experimental data. The source of the discrepancy could not be resolved.

In the case of the phase-change metamaterial model, the modelled spectrum was heavily red-shifted when compared to experiment. Whilst the model showed a red-shift on crystallisation of the GST layer, as in the experiment, the discrepancy between the model and experiment was significant in this case, indicating a significant failing in the modelling technique.

The modelled all-dielectric phase-change metamaterial showed a pronounced change in the spectra between the two phases of the GST, with a remarkably high $Q$-factor resonance in the amorphous phase.

Whilst there were severe discrepancies between the modelled spectra and experiment which could not be resolved, the qualitative red-shifting of the phase-change metamaterial on crystallisation has been demonstrated via modelling. Further, the modelled results of the all-dielectric phase-change metamaterial showed promise; the extent of the modulation of the resonance on changing the phase was much larger than in the case of the phase-change metamaterial. However, only experimental realisation of this structure could verify this.

References


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Chapter 6

Femtosecond GST Switching

6.1 Motivation

Chalcogenide glasses have been cited as a possible medium for all-optical femtosecond switches, as it has been shown that a non-linear refractive index change can occur on a sub-picosecond timescale[6.1]. Crystallisation has been shown to occur on application of single femtosecond pulses[6.2], but controllable and repeatable crystallisation and amorphisation on this timescale is yet to be demonstrated. If this could be realised, then arithmetic and neuromorphic all-optical processing at extremely high data rates could be realised, with the logic performed and result stored in the same medium[6.3].

The feasibility of using femtosecond pulses to display multiple levels of crystallinity in phase-change films was investigated, and reliable crystallisation and amorphisation of marks on these short timescales was demonstrated. If all-optical data processing could be realised in this manner, it could result in a very attractive device.

All work utilising femtosecond pulses was completed in collaboration with Dr. Ben Mills in the Femtosecond Applications of Science and Technology (FAST) Lab.

6.2 Femtosecond-Induced Crystallisation

The laser system consisted of a Coherent Mira laser oscillator pumped by a Verdi V10 which seeded a Legend-F amplifier pumped by a Evolution 30. The system further involves a second and third harmonic generator, an additional optical parametric amplifier and a difference frequency generator, resulting in a wavelength range of 300 nm to 10 µm, pulse durations down to 150 fs and pulse energies up to 10 µJ. The repetition rate of the system was 1 kHz, and it could be run in single-shot mode.
Initial femtosecond pulses were used to excite an area approximately 25µm in diameter in the chalcogenide thin film, to investigate whether repeatable crystallisation was possible with femtosecond pulses. Amorphous films of GST 30 nm thick were sputtered onto quartz substrates, and a 10 nm capping layer of ZnS-SiO₂ was then added on top to prevent oxidation, as in Figure 6.1. This film profile was used for the majority of these experiments, chiefly because 30 nm GST was found to give sufficient contrast on the microspectrophotometer between the amorphous and crystalline states to make them easily discernable.

All the pulses used were 800 nm, 150 fs pulses in the fluence range 5-13 mJ cm⁻². The pulses were shaped to have an approximately ‘top-hat’ intensity profile over an area approximately 25µm in diameter, so that the excited region was of uniform crystallinity, and the area was large enough to obtain a high signal-to-noise ratio on the microspectrophotometer, for an accurate spectrum. The area of uniform switching was also made to be large enough to accommodate a metamaterial region.

Initially, crystallisation of the amorphous film was attempted using continuous pulses, which was successful. Figure 6.2 shows both crystallisation, amorphisation and ablation using trains of 1000 pulses with a 35 ms delay between pulses, and the corresponding spectra are shown in Figure 6.3. Crystallisation was attempted with a single pulse, but it was found that the film would either not crystallise or ablate; much finer control over the incident fluence was required.

It has been demonstrated that femtosecond pulses can both crystallise and re-amorphise thin films of GST, with good contrast and no observable damage. Whilst it is known that the crystallisation process indeed occurs on the nanosecond timescale, the energy required for it to occur may be supplied on the femtosecond timescale[6.4].
Figure 6.2: Amorphised, crystallised and ablated spots, viewed in white-light transmission illumination against an amorphous GST background. In figure (a), mark ‘A’ shows re-amorphisation, via high-fluence (10 mJ cm\(^{-2}\)) pulses ‘melt-quenching’ the GST, which is once again the same shade as the amorphous background. Due to an imperfect ‘top-hat’ intensity profile across the spot, the edges of the mark received a lower fluence, and hence have crystallised, turning darker. Mark ‘B’ has been crystallised by lower-fluence (5 mJ cm\(^{-2}\)) pulses. The edges have received a fluence that is below the crystallisation threshold, and hence remain amorphous. Figure (b) shows ablation; particularly high-fluence pulses \((2.29 \times 10^3 \text{ mJ cm}^{-2})\) have ablated the film, leaving behind only substrate.
Figure 6.3: The transmission spectra of the crystalline, amorphous and ablated marks from Figure 6.2, obtained via microspectrophotometry. Acquiring the spectrum of an ablated region (just substrate) saturated the detector, producing erroneous values slightly over 100%, and as such can be taken to be 100% transmission. The amorphous transmission is initially high; crystallisation on low-fluence femtosecond excitation reduces it significantly. High-fluence excitation re-amorphises the film, increasing the transmission again, but not quite back to its original level. The contrast between the crystallised and re-amorphised states is significant.
6.3 Progressive Switching

GST is stable in either its amorphous or crystalline phase below a certain temperature (usually less than 70 °C), which is beneficial in a binary data storage context, but one particularly attractive feature of GST is that its intermediate or partially crystalline states are also stable[6.5]. This opens the door to many potential applications such as multi-level memory and basic logic operations; the chalcogenide simultaneously becomes the processor and the storage medium. Femtosecond-initiated control of these intermediate states would demonstrate the scalability in terms of speed that GST could provide as a high-density memory material. Figure 6.4 demonstrates this progressive crystallisation effect in an identical setup to Figure 6.2, using up to 200 pulses. The transmission spectra of the 8 mJ cm$^{-2}$ series of exposures are given in Figure 6.5.

It has been demonstrated that cumulative crystallisation can be achieved using successive femtosecond-timescale excitations of thin films of GST. Furthermore, the progressive change in dispersion with each additional pulse demonstrates a non-volatile accumulation functionality which can be reset once saturated. This can potentially offer continuous tunability in a hybrid metamaterial device.

![Figure 6.4: Progressive crystallisation in GST. For a pulse fluence of 6 mJ cm$^{-2}$, there are some partially crystalline regions that become visible with increasing pulse number. The pattern is due to ‘ripples’ of non-uniform fluence in the intensity profile of the beam spot; an unfortunate consequence of attempting to switch such a large area. For 8 mJ cm$^{-2}$, these fluence fluctuations sit within the crystallisation window for the material, and the spot displays progressive, partial crystallisation until it become fully crystalline after around 125 pulses. Further pulses appear to have little effect, showing the crystallisation process to be saturated. At 10 mJ cm$^{-2}$, the fluence ripples exceed the re-amorphisation threshold in places, and portions of the mark appear to be re-amorphised; they are a lighter shade. It was confirmed that these regions were not ablated, as they could be re-crystallised using a lower fluence.](image-url)
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6.4 Femtosecond-Timescale Switching of Phase-change Metamaterials

The hybrid phase-change metamaterial device was then exposed to femtosecond pulses of a similar fluence to attempt to switch the chalcogenide in order to radically alter the resonance spectrum of the entire device. This was largely unsuccessful due to the fact that the fluences required to bring about a change in the crystalline fraction in the GST could frequently damage the structure of the resonators milled in the gold layer.

The phase-change metamaterial was produced using the process outlined in Section 2.3.1, only this time 50 nm gold was deposited by e-beam evaporation and patterned via FIB first. Then an additional 10 nm layer of ZnS/SiO$_2$ was added to provide a ‘buffer’ between the gold and chalcogenide. The resulting film stack is shown in Figure 6.6.

The sample was placed on a hot plate at 250°C for 5 minutes, which was a sufficient length of time above $T_x$ to fully crystallise the chalcogenide layer. The spectra for the structure in amorphous and crystalline phases, in reflection and transmission, are given in Figures 6.7 and 6.8 respectively.

Figure 6.5: Microspectrophotometry of exposed spots, showing the decrease in transmission with pulse number from the amorphous state (orange trace) through to the crystalline state (dark green trace). The transition appears to saturate after approximately 125 pulses.
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Figure 6.6: A phase-change metamaterial stack.

Figure 6.7: There is a clear red-shifting of the resonant features in the reflection spectrum on crystallisation; the reflection minimum at 1400 nm shifts approximately 100 nm. The green line refers to the metamaterial spectrum without the phase-change layers, for reference.
A phase-change metamaterial region was then excited with 100 800 nm, 150 fs pulses with a 100 ms delay, at a fluence of 13 mJ cm$^{-2}$. These parameters produced a visible darkening of the phase-change metamaterial stack on a region of unpatterned gold, potentially displaying crystallisation of the chalcogenide. The resultant spectra are presented in Figures 6.9 and 6.10 respectively.

Even though the phase-change metamaterial was identical in design in both the hot plate and pulse-switched cases, the amorphous spectra in both reflection and transmission are quite different initially, with the pulse-excited amorphous sample exhibiting much broader and lower-quality resonance features. The samples for each case were made in different batches, so some variation in the fabrication process could have caused this discrepancy in the initial spectra. Differing layer thicknesses between the two sample batches were thought to be the cause, yet large variations in the amorphous spectra were seen with each new fabrication run, and the low error on the deposition thickness could not account for this. The cause of these variations was not deduced.

However, the hot plate-crystallised PCMM spectra clearly show a red-shifting of the resonance features, whilst the femtosecond-exposed PCMM shows an apparent blue-shift, contrary to expectations. This is attributed to the femtosecond pulse ablating the chalcogenide layer, resulting in a lower-index dielectric environment for the metamaterial.
Figure 6.9: Excitation of the PCMM using femtosecond pulses appeared to cause the resonance features to blue-shift, contrary to expectations. The reflection minimum at 1600 nm appears to shift to around 1400 nm.

and hence the blue-shift. Damage to the resonators in the gold film as a result of the pulses could also potentially cause this blue-shift of the resonance features in the femtosecond-exposed case.
6.5 Single-Shot Switching

Single-shot femtosecond switching of the PCMM would be extremely attractive in a device due to the high data write rates attainable, as well as displaying the robustness of the system. The main concern was that the high intensities of a single-shot pulse necessary to crystallise the chalcogenide would ablate the adjacent gold layer, or at least damage the metamaterial structuring in some way. A slightly different phase-change stack was constructed, as shown in Figure 6.11, with the gold layer on top; this made any damage to the gold layer instantly clear under viewing via SEM, whilst offering similar resonance shifting functionality as the previous stack in Figure 6.6.

After investigation of the structures in Figures 6.12 and 6.13 using the microspectrophotometer, it was found that there had been no shifting of the resonances in either case. The PCMM in Figure 6.12 displayed no change in the spectrum, and Figure 6.13 showed only broadening and reduction of the quality factor. This can be attributed to the amorphous chalcogenide layer not being crystallised, and the gold layer being damaged due to the extremely high intensity of the single femtosecond pulse.
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Figure 6.11: The phase-change metamaterial stack used for single-shot femtosecond investigations.

![Diagram of the metamaterial stack](image)

- 50nm Au (patterned)
- 10nm ZnS/SiO2
- 30nm GST
- Quartz substrate

Figure 6.12: A 31µm square array of ASRs after a single 4 uJ pulse. No obvious damage to the metamaterial structure is visible.

(a) A 31µm square array  (b) Close-up

It can therefore be concluded that single-shot femtosecond switching of the phase-change metamaterial structure is not possible, as the high absorption of the gold at this wavelength (and relatively low melting temperature) result in damage to the metamaterial structure before the chalcogenide can be crystallised significantly.
Figure 6.13: A 31µm square array of ASRs after a single 5 uJ pulse. There has been considerable damage to the milled gold layer, which will detrimentally affect the quality factor.

6.6 Femtosecond Crystallisation and Re-Amorphisation of PCMMs

To avoid damage to the gold layer, large numbers of low-fluence pulses were used to attempt to crystallise the GST in the PCMM without permanent damage to the gold. The low-fluence crystallisation pulse train consisted of 200 5 mJ cm$^{-2}$ pulses with a delay of 35 ms, and the high-fluence amorphisation pulses consisted of a single 10 mJ cm$^{-2}$ pulse.

As shown in Figure 6.14, crystallisation results in a red-shift of approximately 100 nm, as would be expected due to the refractive index increase in the GST on crystallisation. On amorphisation, the resonance position blue-shifts back to approximately its original position, although there is some damage, made clear by the heavily reduced quality factor. Nevertheless, it has been demonstrated that a reversible wavelength-shift in the PCMM can be produced using two different regimes of femtosecond pulses.
Figure 6.14: A PCMM was crystallised by 200 low-fluence pulses, red-shifting the resonance features. A single high-fluence pulse then re-amorphised the phase-change layer, blue-shifting the resonance features back to their original spectral position. The quality factor of the resonance was reduced however, possibly due to damage to the metamaterial structure as a result of the high fluence.

6.7 Conclusions

Investigating femtosecond-timescale optical switching of phase-change metamaterials was intended to demonstrate the speed and durability of the device under the intense excitation of a femtosecond pulse. Crystallisation and amorphisation in GST were demonstrated using successive femtosecond pulses, and finer control over the pulse power demonstrated progressive crystallisation in the crystalline marks. Femtosecond pulses incident on the phase-change metamaterial structure appeared to damage the gold structuring before any evidence of crystallisation in the phase-change layer was seen, resulting in a blue-shifting of the resonance and a reduction in the $Q$-factor. Results with single-shot crystallisation attempts showed similar damage to the gold structuring.

Using high numbers of lower-fluence pulses, the GST was apparently crystallised, resulting in a red-shift in the resonance spectrum. A single higher-fluence pulse then appeared to amorphise the GST, resulting in a blue-shift of the resonance back to its original amorphous position, albeit with a reduction in $Q$-factor. In conclusion, femtosecond pulse-induced switching of the phase-change metamaterial device, whilst displaying an
REFERENCES

element of reversibility, appears limited by the rapid failure of the gold structuring. The high absorption of the gold film combined with the pulse fluence required to crystallise and amorphise the phase-change layer result in damage to the gold nanostructuring, and hence a rapid reduction in quality-factor of the entire device on successive switching operations. A system such as the proposed all-dielectric phase-change metamaterial would therefore potentially be more robust on application of femtosecond pulses.

References


Publications and Conferences


