This chapter presents a brief introduction to the field of data storage with phase-change materials. The various aspects of this technology (viz. motivation, current trends and challenges) are reviewed.

1.1 Amorphous materials: an introduction

Amorphous materials are interesting materials to study from a fundamental point of view as they present challenging and as yet unsolved problems in the field of condensed matter physics. These materials have widespread use in our lives with applications ranging from primitive obsidian weapons to optoelectronics. Today, every office in the world contains storage media for computers (for example DVD-RW compact disks) that utilize the special reversible laser-driven amorphization/crystallization transition properties of a particular GeSbTe glass (Kolobov et al. 2004). The same computer uses crystalline Si chips that depend critically upon the dielectric properties of a-SiO$_2$ (Feinberg 1999). With increasing pressure on global energy markets, it is notable that some of the most promising photovoltaic devices are based upon amorphous materials such as a-Si:H because of the low cost of the material (compared to crystalline devices) and the ability to grow thin films of device-quality material over wide areas (Singh 2005). The internet depends upon fiber-optic glass light pipes that enable transmission of information with bandwidth vastly exceeding that possible with wires (Danesh and Pantchev 2000).

Amorphous materials exist in the structurally interesting region between crystals and liquids. These materials are characterized by the random arrangement of the atoms and absence of long range order. This absence of long range order is the essential aspect, which makes them differ from their crystalline counterparts (Figure 1.1). The arrangement of atoms, however, will not be entirely random as in gas. The binding forces between atoms are very similar to those in the crystal and although, long range order is excluded, short range order of few lattice constants will generally be present. Amorphous materials can be in two forms: either as viscous liquids or glasses. A glass is a disordered material like a viscous liquid but which behaves mechanically like an isotropic solid. When a liquid (melt) is cooled, one of two events may occur. Either crystallization may take place at the melting point $T_m$, or else the liquid will become ‘supercooled’ for temperature below $T_m$, becoming more viscous with decreasing temperature, and may ultimately form glass. These changes can be observed readily by monitoring the volume as function of temperature as shown in figure 1.2.
Figure 1.1  Structure of (a) crystalline and (b) amorphous semiconductors.
The crystallization process is manifested by an abrupt change in volume at $T_m$, whereas glass formation is characterized by gradual break in slope. The region over which the change of slope occurs is termed as ‘glass transition temperature’ $T_g$ (Elliot 1990). Practically any liquid crystallizes if the cooling rate is sufficiently slow; hence there is a critical cooling rate above which a liquid can be vitrified. On cooling the viscosities of liquids gradually increase (Kittel 1996): by general agreement it is considered that a liquid on being cooled becomes a glass when the viscosity equals $10^{12}$ Pa s ($10^{13}$ poise) or where the relaxation time is $10^2$ s (Kittel 1996, Richert 2002). The liquid–glass transition is accompanied by spectacular changes in physical properties (e.g. glasses are rigid whereas supercooled liquids are soft); however, no obvious changes occur at the molecular level and the material is topologically disordered both in liquid and glassy states Roland and (Casalini 2005). Amorphous semiconductors are a unique class of materials that have transformed society and technology in truly revolutionary ways. A reasonably large number of different semiconductor materials are used in various electronic and electro-optical devices. They are broadly divided into two types, i.e., tetrahedrally bonded amorphous semiconductors (Si, Ge) and chalcogenide glasses (Se, As$_2$Se$_3$). Based on the above classification these materials are listed in Table 1.1.

**Tetrahedrally-Bonded Semiconductors:** These compounds are either of the III-V type (e.g., GaAs, InP) or the II-VI Type (e.g., CdTe, ZnS). Thus, eight atoms are available ($3+5 = 8$ or $2+6 = 8$) to be shared by the atoms. Four covalent bonds per atom are generally formed. They have wide range of applications such as in solar cells, thin film transistors, sensors etc.

**Chalcogenide Glasses:** The three elements S, Se and Te of group VI with a valance shell of $ns^2np^6$ are known as chalcogens. The common factor linking chalcogen elements is the presence of six electrons in their outer valence shell. When neutral, the atoms have two electrons paired in a filled $s$ shell, two more in a filled $p$ shell, and one each in the other two $p$ shells. This configuration leaves two unfilled states in $p$ orbitals to participate in the formation of chemical bonds. Thus, these atoms tend to form structures in which the chalcogen atom has two covalent chemical bonds. With only two bonds, the atoms are relatively free to move by rotating around the axis between the two bonding atoms. The bond angle at the chalcogen atom is also flexible and the bond can easily open or close by several degrees. In a solid, an additional constraint to motion is provided by ionic and Van Der Waals interactions with neighboring atoms. The flexibility of chalcogenide chemical
Figure 1.2  The volume-temperature diagram for glass forming systems; $T_g$: glass transition temperature, $T_m$: melting temperature.
Table 1.1 Classification of amorphous semiconductors.

<table>
<thead>
<tr>
<th>Tetrahedrally-Bonded Semiconductors</th>
<th>Chalcogenide Semiconductors</th>
</tr>
</thead>
<tbody>
<tr>
<td>C, Si, Ge</td>
<td>S, Se, Te</td>
</tr>
<tr>
<td>SiC, InSb, GaAs, GaSb</td>
<td>As$_2$S$_3$, As$_2$Se$_3$, As$_2$Te$_3$</td>
</tr>
<tr>
<td>Ge-Sb-Se, As-Se-Te, Ge-Sb-Te</td>
<td></td>
</tr>
</tbody>
</table>
bonds causes these atoms to readily form amorphous networks either alone, or with a variety of other atomic constituents. Binary glasses can be formed that contain the heavier Group IV and V elements and some of the Group VII elements (Borisova 1981). Binary mixtures with germanium and arsenic are the most commonly studied because they have large glass-forming regions, especially when selenium is the chalcogen atom. Increasing the number of components tends to increase the glass-forming range (Borisova 1981), and ternary glasses have been formed with components from every column of the periodic table (Mott and Davis 1979). Typically, any amorphous material containing an abundance of chalcogen atoms is referred to as a chalcogenide glass. As$_2$S$_3$ was the first material which was studied as a chalcogenide material for near and middle infrared region of the electromagnetic spectrum. Later, semiconductor properties and switching phenomenon were observed in these materials. Presently these materials are extensively explored for middle and far infrared region and for data storage applications.

1.2 Information storage

From the ancient times, man used to collect information and store it; old petroglyphs (carving or line drawing on rocks, especially one made by prehistoric people) are the proof of his quest for storing data. The continuous efforts for searching better ways to store data lead us to today’s information technology, which includes the office/home computer, mobile phones, web servers, digital note books, i-Pods, CD’s, DVD’s. Such a wide range of applications results in a wide range of commercially available data storage technologies, each tailor-made for a specific application. These technologies differ in specific properties such as the storage capacity and density, the throughput (the speed at which data can be written, read and erased), the cyclability which denotes the number of write-erase cycles that can be performed by a storage device, the life-time, the volatility (whether the stored data is lost if the supply with electric power is cut off) and of course the costs of the technology. The different types of data storage techniques used nowadays are discussed briefly in the next section.

1.2.1 Types of memories

Magnetic storage: In computer hard disk drives data is stored in the magnetization direction of small bits on a ferromagnetic surface. This storage technique is nonvolatile. The information is accessed using read/write heads. Since the read/write head only covers a part of the surface, magnetic storage is sequential access, i.e. the head has to be
positioned correctly in order to access the data. Therefore this storage technique is rather slow.

**Semiconductor storage:** It uses semiconductor-based integrated circuits to store information. The DRAM used to hold data in a computer during computation consists of capacitors of which each separately stores data. It provides random access to the information, i.e. any location can be accessed at any moment in the same amount of time. The DRAM is characterized by a high throughput and a high storage density. However, in contrast to the hard disk drive the DRAM device is a volatile storage device, i.e. its data is lost when the power supply is switched off.

**The flash memory** provides non-volatile semiconductor storage. It is widely used today in various electronic devices such as mobile phones, pda's, usb-drives or digital cameras. The drawbacks of this technology are poor cyclability and long read/write times. Although it is highly desirable to replace DRAM devices in personal computers by non-volatile memory technologies, but due to above mentioned drawbacks, flash memories are prevented from being employed in this field.

**Optical disc storage** uses pits etched on the surface of a disc to store information. The data is read by illuminating the surface with a laser and measuring the reflection. This technology is non-volatile and employs sequential access. Several standards are available today: CD, DVD (read only storage), CD-R, DVD-R (write once storage), CD-RW, DVD-RW, DVD-RAM (write and erase). In read only storage systems, the data is written by molding pits onto the storage layer. In the writable storage systems it is written on the surface by the same laser beam which is used for reading, however employing higher intensity in order to change the state of the surface, e.g. from the crystalline to the amorphous phase. Similar to the magnetic hard disk it requires movable parts, which makes it less shock-resistant and thus less suitable in portable devices than the flash memory.

### 1.2.2 Future concepts in memory technologies

The Magnetoresistive-RAM (MRAM), the Ferroelectric-RAM (FeRAM) and the Phase-Change-RAM (PCRAM) are among the most promising candidates for data storage.

**MRAM** uses magnetic rather than electrical structures to store information, so it does not need to be constantly powered to retain data, like DRAM technologies. In MRAM devices, magnetic fields are generated at intersections on a grid of power rails. When current travels
through a power rail which is opposing the polarization of one of the magnetic field bits, its current flow is diminished and the bit value stored by the field is detected by this weakened current flow.

**FeRAM's** employ ferroelectric capacitors. Each capacitor consists of a crystalline cell containing one specific atom which has two stable positions. The information is then stored in the orientation of the electric dipole in the cell, which is retained even without an external field. Thus FeRAM's possess the two characteristics required for a non-volatile memory cell, i.e. they have two stable states and they retain their states without electrical power.

**PCRAM's** the change in electric conductivity upon phase transition from crystalline to amorphous structure is exploited to store information. The same concept is used in current optical data storage devices such as DVD-RW or DVD-RAM. The difference in the optical properties between the crystalline and the amorphous state is usually referred to as the optical contrast of the material.

### 1.2.3 Comparison of different memories

Ideally, the need is for technologies that combine higher density with the fast read/write speed of synchronous RAM, the lower cost of dynamic RAM, and the non-volatility of Flash memory, which can store data when a device is turned off. Among alternative non-volatile memory (NVM) concepts like Fe-RAM and M-RAM, that have been under investigation since a few years, Phase Change Memories (PCRAM) have more recently received sustained interest, since their early proposal (Ovshinsky 1968) in late '60, and now are considered one of the best candidates for next generation NVM, due to improved performances compared to Flash (access time, read throughput, direct write, bit granularity, endurance) as well as to their good scalability within current CMOS fabrication methodology (Wicker 1999, Lai and Lowrey 2001, Hwang et al. 2003, Pellizzer et al. 2004) (Table 1.2).

### 1.3 Phase change memory: A brief Introduction

First floppy disks formed the basis of nonvolatile rewritable memory then, Flash memory took on changing the realm for better, but soon the two may be forgotten, as the time is here to make way for the fast performance memory device of the future – the phase change memory. Some important phenomena to describe the phase change process are summarized before we proceed with the present study. Phase Change Memories are based on the
Table 1.2  Comparison of data storage technologies (Wicker 1999, Lai and Lowrey 2001, Hwang et al. 2003, Pellizzer et al. 2004).

<table>
<thead>
<tr>
<th></th>
<th>Volatile/Non-Volatile</th>
<th>Scalability</th>
<th>Endurance Read/write/erase cycles</th>
<th>Data retention</th>
<th>Write time</th>
<th>Write power/Bit (V×I)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DRAM</strong></td>
<td>Volatile</td>
<td>Fair</td>
<td>Unlimited</td>
<td>10 ms</td>
<td>&lt;100 ns</td>
<td>3V×100µA</td>
</tr>
<tr>
<td><strong>FLASH</strong></td>
<td>Non-Volatile</td>
<td>Fair</td>
<td>$10^2$</td>
<td>&gt;10 years</td>
<td>µs/ms</td>
<td>5V×1mA</td>
</tr>
<tr>
<td><strong>Fe-RAM</strong></td>
<td>Non-Volatile</td>
<td>Poor</td>
<td>$10^{10}$</td>
<td>&gt;10 years</td>
<td>&lt;100 ns</td>
<td>3V×100µA</td>
</tr>
<tr>
<td><strong>M-RAM</strong></td>
<td>Non-Volatile</td>
<td>Poor</td>
<td>&gt; $10^{18}$</td>
<td>&gt;10 years</td>
<td>&lt;100 ns</td>
<td>1.8V×10mA</td>
</tr>
<tr>
<td><strong>PCRAM</strong></td>
<td>Non-Volatile</td>
<td>Good</td>
<td>$10^{12}$</td>
<td>&gt;10 years</td>
<td>&lt;100 ns</td>
<td>3V×1mA</td>
</tr>
</tbody>
</table>
reversible phase transition of a chalcogenide material that can be reversibly switched between crystalline and amorphous state. Present day data storage media (viz. CD-RW, DVD+/-RW and PCRAM) stores the data in a single spot of amorphous phase in crystalline surrounding. Amorphous spot refers to digitally high value ‘1’ whereas crystalline surrounding represents the digitally low value ‘0’. Depending on the mode of operation phase change storage media can be divided into two categories (i) electrical erasable phase change memories (ii) optical phase change memories. In electrical erasable phase change memories an electrical current pulse is used to switch between amorphous and crystalline phases. It uses the difference in electrical resistance to store the data bit, because the phase change media shows very high resistance in amorphous phase than in crystalline phase. The optical data storage media takes the advantage of high difference between the reflectivity of amorphous and crystalline phase. A laser pulse is used to switch between the two phases. An amorphous spot in the crystalline surrounding act’s as the stored bit.

**Phase change materials**

Phase change materials are those which show significant change in the electrical and optical properties on phase transformation. These materials crystallize in single phase thus the time for crystallization is of the order of nanoseconds. The change in reflectivity in these materials is about 30% on phase transformation. Currently applied phase change media are mainly based on ternary GeSbTe alloys and quaternary AgInSbTe alloys (Yamada et al. 1991). Four types of ternary alloys of Ge$_2$Sb$_2$Te$_5$, Ge$_1$Sb$_4$Te$_7$, Ge$_1$Sb$_2$Te$_4$ and Ge$_3$Sb$_7$Te$_5$, formed with compositions along the GeTe-Sb$_2$Te$_3$ tie-line, have been identified. Among them most studies have focused on Ge$_2$Sb$_2$Te$_5$ (GST) due to its excellent properties with respect to reflectivity contrast, cyclability, stability and crystallization speed (Kolobov et al. 2004, Wang et al. 2004).

**Fast amorphous to crystalline phase transformation in GST**

Amorphous-crystalline transformation in GST is fast and stable due to the absence of the rupture of covalent bonds during the above process (Kolobov et al. 2004). The model presented by Kolovov et al. 2004 provides a clear explanation of rapid amorphous-crystalline transformation in GST. There is a significant similarity between the structures of Se and Te and the structure of GST. In both cases, there are two kinds of bonds. In Se (Te) there are stronger covalent (intrachain) bonds and weaker van-der-Waals (interchain) bonds. Upon amorphization, the weaker van-der-Waals bonds break and the interchain
bonds dominate the local structure getting stronger and shorter. A similar bond hierarchy also exists in GST where shorter (stronger) Ge(Sb)–Te bonds co-exist (Kolobov et al. 2006).

The structure of GST in the crystalline state is a distorted rocksalt structure. Upon amorphization, disordering of the covalent network does not take place. Instead, amorphization is primarily due to a switch of Ge atoms from octahedral symmetry positions into tetrahedral symmetry positions without rupture of strong covalent bonds. The driving force for the transition is the presence of strained Ge–Te bonds, the relaxation of which releases energy sufficient for the Ge atom to travel across the plane separating octahedral and tetrahedral symmetry sites. It is this nature of the transformation that ensures fast disk performance and repeatable switching over millions cycles as well as large changes in reflectivity.

A 63 atom model of Ge$_2$Sb$_2$Te$_5$ obtained from computer simulations has been reported by Hegedus and Elliott (2008) (Figure 1.3 a). In Ge$_2$Sb$_2$Te$_5$, Te atoms form fcc lattice and Ge occupies octahedral and tetrahedral positions in the crystalline and amorphous states respectively. Positions of Ge and Te in crystalline and amorphous states are shown in Figure 1.3 (b). At amorphous to crystalline transformation temperature, with the rupture of weak bonds, Ge flips into the tetrahedral position. Whereas on melting the Ge atom undergoes a reverse (umbrella) flip to octahedral position resulting in the distortion of the Ge sub lattice (Kolobov et al. 2005). The Sb atoms mainly play the role of enhancing overall stability of the metastable crystal structure by participating in the overall electron balance (Kolobov et al. 2005).

1.4 Phase change memories: phenomena and characteristics

In optical data storage, a focused laser beam is applied, to switch micron sized bits between the crystalline and the amorphous state. This concept is shown in figure 1.4. The information is written by locally melting the crystalline material and rapidly quenching it. This results in an amorphous bit. Erasure is achieved by heating this amorphous region above the crystallization temperature. The current state of a region on the storage device is subsequently read by a laser pulse of low intensity. In the PC-RAM's advantage is taken of the change in electric conductivity upon the phase transition from the crystalline to the amorphous structure (Hudgens and Johnson 2004, Greer and Mathur 2005, Lankhorst et al. 2005). Here the write-read-erase-cycle is affected by an electrical pulse. Figure 1.5 and 1.6 show the schematic cross section of a PCRAM cell and the corresponding current-voltage curves. The cell is essentially a nonlinear resistor and the readout is performed at low bias (READ region in figure 1.6), where the low-field resistance changes
Figure 1.3 (a) Amorphous (left) and crystalline (right) structures of a 63 atom model of Ge$_2$Sb$_2$Te$_5$, obtained from computer simulations. Colours: Ge - green, Sb - red, Te - blue. (Hegedus and Elliott 2008)

(i) Crystalline state

(ii) Amorphous state

Figure 1.3 (b) Switching of Ge atom (shown as red circles) from an octahedral symmetry position in crystalline state (i) into tetrahedral symmetry position in amorphous state (ii).
Figure 1.4 Functional concept of Phase change materials
Figure 1.5  Schematic diagram of a phase-change memory cell. Depending on the state of the active region (crystalline or amorphous), the resistance of the cell changes by several orders of magnitude. (Welnic and Wuttig 2008)

Figure 1.6  Current–voltage curve for a phase-change memory cell. SET and RESET denote the switching regions, while READ denotes the region of readout. (Welnic and Wuttig 2008)
by orders of magnitude depending on whether the PCM in the active region of the device is crystalline or amorphous. To reach the switching regions (SET and RESET in figure 1.6) the bias is raised above the switching voltage so that enough current can flow through the cell, heating up the active region (Figure 1.5) resulting in the crystalline-amorphous phase-change (Pirovano et al. 2005a, Pirovano et al. 2005b). The basic cell is composed by a thin chalcogenide layer in contact with a metallic element, usually called heater, which forces the high current densities and the high temperatures required for phase transitions, in the GST region close to the heater interface, named PCM active area.

At present several manufacturers of RAM chips have initiated research and development projects to explore and use the potential of non-volatile storage with phase change materials. The electric switching employed in PC-RAM’s is accompanied by a so called threshold switching (Adler et al. 1978). At low voltage the amorphous state switches from a highly resistive to a conductive state, which is however still amorphous, followed by a memory switch from the amorphous to the crystalline state. In this way the material changes locally between two states characterized by very different resistance values. Both switching processes –the change in resistance and the following amorphous-crystalline phase transition- are just as the optical contrast not fully understood.

**Special materials**

It is very difficult to believe that a material will stand millions of melting/solidification cycles without degradation of parameters and an essentially specific mechanism should be found. The fundamentals of the phase-change mechanism are just starting to emerge but striking features of both groups of materials are: (i) the existence of longer and shorter bonds between similar pairs of atom types in the crystalline state (Matsunaga et al. 2001, Kolobov et al. 2004), (ii) bond shortening in the amorphous state (Matsunaga et al. 2001, Tani et al. 2001, Kolobov et al. 2004), and (iii) a considerable degree of intrinsic disorder, manifested in high concentrations of vacancies in GST (Yamada and Matsunaga 2002) and a random occupancy of sites in AIST (Matsunaga et al. 2001). The first feature suggest that certain bonds in the system are weaker and can be selectively broken, the second one is an indication of the local atomic structure in the two states being significantly different, and the last property points to a considerable concentration of defect levels in the gap.
1.5 History of development of PCM technology

First research on chalcogenide glasses in 1950, was focused on As$_2$S$_3$, an optical material for near and middle infrared region of the electromagnetic spectrum. In 1960, electrical properties of some chalcogenide glasses were studied by (Eaton 1964, Ovshinsky 1968, Pearson 1969) and observed their semiconductor properties and switching phenomenon. At the beginning of 70's the research was split in two directions: the first one was dedicated to the optical materials for middle and far infrared region of the electromagnetic spectrum (for example As$_2$Se$_3$, Ge-As-Se, Ge-Se-Te) and, the second one was dedicated to the materials exhibiting threshold and memory switching phenomenon (this direction started with amorphous layers containing tellurium, e.g., Ge$_2$Sb$_2$Te$_5$, AgInSbTe etc.).

Many materials can be melt quenched to form an amorphous state, but only few of them possess a marked difference in optical properties between the amorphous and crystalline state. Hence, only a very few materials have the unique property combination found in phase change materials used for optical storage. The large optical contrast indicates that the atomic arrangement differs considerably between the amorphous and crystalline states. On the other hand, the atomic rearrangement required on recrystallization proceeds very fast (on a timescale of ten to one hundred nanoseconds) (Chen et al.1986, Yamada et al. 1987). It is interesting to note that the required contrast in electrical conduction is much easier to meet, so there might be many more candidates for non-volatile memory than for rewriteable optical storage.

Most of the materials fail to meet one or other requirements viz. (i) High-speed phase transition, (ii) Long thermal stability of amorphous state, (iii)Large optical change between the two states (for rewriteable optical storage), (iv)Large resistance change between the states (for non-volatile electronic storage), (v) Large cycle number of reversible transitions and (vi) High chemical stability. Thus challenge is the systematic identification of materials that can fulfill the above mentioned conditions. The question thus arises of how to identify materials. Suitable materials for rewriteable optical storage that have been identified in the past few decades are briefly discussed in the next paragraph.

The first materials used were as Te-based eutectic alloys, represented by Te$_{85}$Ge$_{15}$, doped with elements such as Sb, S and P. These materials were good glass formers (Ovshinsky 1968). Although these materials already showed electrical switching that could be used for electronic storage, but these alloys did not crystallize in a single-phase material.
and thus time for crystallization was of the order of microseconds. The first materials to show fast recrystallization and good optical contrast were GeTe (Chen et al. 1986) and Ge$_{11}$Te$_{60}$Sn$_4$Au$_{25}$ (Yamada et al. 1986, Ohno et al. 1989). This triggered the discovery of pseudo-binary alloys along the GeTe–Sb$_2$Te$_3$ tie line, such as Ge$_3$Sb$_4$Te$_7$, Ge$_3$Sb$_2$Te$_4$ and Ge$_2$Sb$_2$Te$_5$ (Yamada 1987, Yamada et al. 1991). Nowadays Ge$_2$Sb$_2$Te$_5$ and related materials such as GeSbTeN, GeSnSbTe, GeBiSbTe, GeBiTe and GeInSbTe (Kojima et al. 1998, Kojima and Yamada 2001, Yusu et al. 2005, Kusada et al. 2006) have been tried, some of which are frequently used in commercial products. A second material family of doped Sb$_2$Te alloys was found later, in which dopants such as Ag, In and Ge have often been used (Iwasaki et al. 1992, Horie et al. 2000, Kato et al. 2002). A composition close to Ag$_5$In$_5$Sb$_{60}$Te$_{30}$ (AIST) is frequently used in rewriteable optical storage media such as DVD-RW and DVD+RW (Iwasaki et al. 1993). In recent years a third material family has been found (Afonso et al. 1992, Yuzurihara et al. 2005) that uses Ge-doped Sb.

1.6 Challenges

The important aspects of a successful rewritable storage media include a large memory capacity (high density data storage), fast phase transformation between the amorphous and crystalline phases (high speed data transfer), large number of reversible transitions (large number of overwrite cycles), prolonged thermal and chemical stability of the phases at room temperature (mark stability), large optical reflectance or electrical resistance difference between the two phases (high signal to noise ratio) (Sang et al. 1999). Therefore, the above mentioned key factors are of great importance for the development of phase-change data storage technology. In the following sections these essential issues are briefly discussed.

1.6.1 High storage capacity

Today’s phase-change memories (e.g. CD-RW, DVD-RW and Blu-ray discs) use a laser beam for data recording. In this optical recording technique, reducing the spot size of the laser (used for data writing) will reduce the written mark (or bit) and hence lead to higher data densities. There are two ways to reduce the spot size, (i) reducing the wavelength ($\lambda$) of the laser and (ii) increasing the numerical aperture (NA) of the objective lens (which focuses the laser beam), because of the size of the (diffraction limited) laser spot is proportional to $\lambda$/NA. Most efficient way is using short wavelength lasers (moving to blue-violet regions) together with lenses having large numerical apertures (using solid
immersion lenses and near-field optical technologies). (Schep et al. 2001) achieved 22.5 GB rewritable digital versatile recording discs using a blue laser ($\lambda = 405$ nm) and a lens with $\text{NA} = 0.85$.

The second way to increase the data storage density is by dual-layer recording as proposed by Nagata et al. (1999).

Figure 1.7 shows the development in data storage density of the phase change optical recording technology. Comparing the first (CD-RW) and recent (BD-RE) version of the optical disc format, the data density has been increased almost 100 times. Yet another way to increase the storage density is multilevel recording. This was first announced in a phase-change electrical memory device in 1997 which showed 16 switching levels and later in 2001, O’Neill showed 8 level phase-change recording technology, which enabled 2 GB of capacity on a CD-RW disc. In phase-change optical recording, this multilevel recording is realized by modulating the reflectivity level. The storage capacity is at present increased to 50 GB by using the combination of blue laser, high NA and a dual-layer. This capacity is higher than the required capacity of 45 GB needed to replace the video tape recorders.

Near-field systems have also been proposed to increase storage density including solid immersion lenses with $\text{NA}$ larger than 1, and super-hemispherical solid immersion lenses (Ovshinsky 1997, Tominaga et al.1998). The air gap between a rotating disc and a near-field optical head is only 50 nm. This led to development of other types of near-field systems, such as super resolution near-field structure (super-RENS, Figure 1.8) which allows the writing and reading of mark size considerably below the size of the laser wavelength used (Tominaga et al. 1998).

In this case a masking layer is used above the storage layer. Super-RENS is unique in that the near-field aperture is fabricated in the optical disc itself, for example, a Sb thin film. As can be seen from the figure, in addition the GST layer sandwiched between two capping layers there is another layer, Sb in this case, which acts as a masking layer. When a laser pulse hits the structure, Sb heats up. Since the intensity in the beam has Gaussian distribution, the central part is heated to a higher temperature. When heated, the Sb layer becomes transparent, i.e. an aperture opens in it which serves as a near field source. The distance between the light source and the recording media is now fixed and determined by the thickness of the capping layer between the masking layer and the GST layer. With
Figure 1.7  Technological evolution in phase-change optical recording showing various disc structures with enhanced data densities. Laser wavelength is reduced from 780 nm (red) to 405 nm (blue-violet), Numerical aperture of the objective lens system is increased from 0.5 to 0.85. The mark size is reduced from about 800 nm to 150 nm i.e., the data density is increased about 7 times going from CD to DVD and about 10 times going from DVD to the dual-layer Blu-ray rewritable (BD-RE) discs. (Wuttig and Yamada 2007)
Figure 1.8  A schematic presentation of transmission Super-RENS.
(Kolobov and Tominaga 2002)
optimized parameters for each layer, the aperture in the Sb layer opens for the time sufficient to record a bit into the GST layer.

When the disk rotates and the exposed Sb spot moves away from the light, the aperture closes. A similar process takes place during the read-out stage. This kind of Super-RENS is called transmission Super-RENS and bits with the size considerably below the diffraction limit have been successfully recorded (Timinaga et al. 1998, Nakano 1999). An alternative design contains an AgO$_x$ layer (instead of the Sb layer). Light causes reversible decomposition of AgO$_x$ and the formation of Ag nanoparticles. Local plasmons excited by light in these particles emit optical near-field. This technical design is usually referred to as scattering type Super-RENS (Tominaga et al. 2000). The latter structure was demonstrated to be a basis for a purely optical photonic transistor (Tominaga et al. 2001).

In phase-change electrical recording, effective reduction of memory cell size will enhance the data density. However, the cell size cannot be reduced below certain limits (about 50 nm) because of many physical constraints at nanoscale level including: (i) fabricating the cell and its electrode contacts and (ii) equipping supporting electronic components of the cell. Atomic force microscopy (AFM) or probe-based data recording has emerged as an alternative technology to achieve ultrahigh data densities. This technology shows several attractive features including the following: (i) producing mark smaller than 20 nm size is readily possible, (ii) writing, reading and erasing operations can be performed with same apparatus (Kado and Tohda 1995, Kado and Tohda 1997, Saluel et al. 1999, Gotoh et al. 2002, Tanaka et al. 2004, Gidon et al. 2004, Lin et al. 2006, Hamann et al. 2006) and (iii) high recording speed is also achievable by using a large number of sharp tips together (Vettiger et al. 2000). Because of its versatile nature this technology is emerging as a promising candidate among the other phase-change recording methods, to produce high data storage densities.

A successful phase-change memory requires high data storage capacity must be accompanied by faster data transferring rate. Therefore the next section briefly presents the data transfer rate of a phase-change memory and the related developments.

1.6.2 High data rate-reading, writing and erasing

Data transfer rate of a phase-change media is related to amorphization and crystallization rate of its recording material. Amorphization process of the phase-change recording material is generally a much faster process (t << 1 ns) than the crystallization. Therefore,
crystallization becomes the rate limiting process i.e., the maximum achievable data transfer rate of a phase-change media is determined by the crystallization kinetics of the phase-change material. Generally, crystallization involves two steps namely; (i) crystal nucleation and (ii) crystal growth in phase-change materials. This means that by accelerating the crystal nucleation and/or growth processes, increased crystallization rates can be obtained. A number of ways have been reported on how to increase the crystallization rate. One option is to use stoichiometric phase-change materials which crystallize into a single-phase, so that any time consuming diffusion processes associated with phase segregation are excluded (Borg and Schijndel 1999). The other options are (i) adding dopants (e.g. N and O) to the phase-change material to enhance its nucleation and (ii) sandwiching the phase-change film between the nucleation promoting (dielectric) layers such as SiC, GeN and GeCrN. Very small quantities of dopants are added confirming that they do not have any decelerating effects on the growth rates.

In figure 1.9, the (multi) layer structures of a conventional (a) and modified (b) phase change optical disc are shown. Frequently used sandwiching or capping layer materials are GeCrN, Si₃N₄ and a mixture of ZnS and SiO₂. GeCrN was developed to improve the nucleation rate and also to serve as an interface layer between the phase-change and other dielectric layers. The interface layer is also crucial to prevent the possible sulfur diffusion into the phase-change film form the sulfur containing dielectric layers such as ZnS-SiO₂. It should be noted that the above motioned methods to improve the nucleation rate are based on the growth-driven (GeSbTe) materials and may not be compatible for the nucleation-driven (doped SbTe) materials. Data transfer rates as high as 80 Mbps have been demonstrated in six layer stacked optical disc structures (Yamada et al. 1998, Zhou and Jacobs 1999, Borg et al. 2001, Tieke et al. 2000). However, these rates are still considerably below the required rate (100 Mbps) for handling the high definition television (HD-TV) signals.

1.6.3 Data Storage capacity and transfer rate

Figure 1.10 summarizes an overview of the phase-change recordings in the bit size (storage capacity) and write, erase speed (data transfer rate/response time). In the beginning when (Ovshinsky 1971) explored reversible amorphous-crystalline transitions in GeTeSbS, a mark size was the order of a few microns and long response times in the range between µs and ms, making the materials not attractive for practical usage. Then later, (Yamada et
Figure 1.9  (a) Schematic of the layer stack in a conventional phase-change optical disc, where a polycarbonate substrate contains 1: 1st dielectric layer, 2: phase-change film, 3: 2nd dielectric layer and 4: reflective (Al-based) layer. (b) Schematic of the layer stack in a modified disc. This is designed to improve the data transfer rate and overwrite cyclability by introducing interface layers between the phase-change film and dielectric layers. The layers on the polycarbonate substrate are 1: 1st dielectric layer, 2: 1st interface layer, 3: phase-change film, 4: 2nd interface layer, 5: 2nd dielectric layer and 6: reflective layer. (Njoroge 2001)
al.1991) demonstrated that such slow response during amorphous to crystalline phase transitions is caused by long range atomic diffusion, leading to phase-separated crystalline structures in the nonstoichiometric films. They also discovered a new system, quasibinary GeTe-Sb$_2$Te$_3$, showing response times between 10 and 50 ns due to short range atomic migrations upon crystallization. In addition, short wavelength (blue-violet) semiconductor lasers together with high numerical aperture focusing lens system have reduced the mark size from about 400 to 150 nm.

The expected future trend is that the optical and the electrical storage technologies will progress toward different extremes. The electrical data storage technology is capable of producing 50 to 10 nm marks (3 to 15 times smaller than the laser produced marks), whereas the associated electrical circuits introduce an intrinsic limit to the response time (from ns to µs), which is probably governed by stray capacitance. On the other hand, in the optical recording technology, the laser wavelength will set a mark size limit of about 100 nm, provided using advanced near-field optical technologies (Hosaka et al. 1996, Tominaga et al. 1998). Regarding the data transfer rates in the optical recording, some recent studies have demonstrated that ultra short (picosecond) laser pulses are able to induce (reversible) phase transitions (Ohta and Yamamoto 2001, Ohta 2001, Solis and Afonso 2003, Siegel et al. 2004). Although, such observations do not necessarily suggest that the phase transitions are completed within picoseconds, they confirm the possibility of attaining high data transfer rates. However, it can be predicted that with the future advancements and optimization, both the optical and electrical recording techniques will provide a dramatic progress in the performance of memory devices.

1.6.4 Cyclability
The parameter cyclability means the number of overwrite cycles, which the data storage media can withstand. Overwriting means writing a new mark over an existing one in a single step instead of performing two steps namely, i) erasing the existing mark and ii) writing the new mark. The optical reflectivity contrast between the phases deteriorates for larger number of direct overwrites. Therefore, the overwrite cyclability also becomes one of the important parameters in phase-change optical recording. Various potential factors responsible to this issue are listed below.
1) Local changes in the film thickness and void formation in the film due to material flow along the recording track on laser irradiation (Ohta et al. 1989, Okamine et al. 1992).
Figure 1.10 Historical development of response time and mark size of electrical and optical phase-change recordings. The star represents the present probe based data storage (Tanaka et al. 2004).
2) Sulfur diffusion from the adjacent dielectric layers into the recording layer due to multiple overwriting.

3) Microscopic defects are caused by the induced thermal stresses during the cyclic phase transitions in the recording layer. These microscopic defects accumulate with number of overwrite cycles and subsequently results in optically detectable macroscopic defects, which can reduce the signal to noise ratio (Suzuki et al. 1990, Horie and Ohno 1996).

4) Phase separation or segregation upon repetitive write and erase cycles.

The material flow can be controlled by adding dopants to the phase-change recording layer. The dopant materials are almost the same as those used to modify the crystallization rates. Since the dopants have higher melting points than the phase-change material (implies that dopants are clustered and aggregated which is not necessarily true), they remain in solid form when the recording layer melts upon writing or overwriting processes and suppress the material flow (Ebina et al. 1999, Jeong et al. 2001). Ebina et al. 1999 reported achieving $5 \times 10^5$ overwrite cycles upon adding 6 at.% of oxygen to a GeSbTe film.

As already mentioned earlier, the sulfur diffusion can be solved by introducing interface layers between the phase-change and the sulfur containing dielectric layers. The material for such interface layers include GeCrN, GeN and SiC, which are also the same nucleation promoting layers discussed in the previous section. Because of their high hardness, high chemical stability, high melting point and highly closed structures, the interface layers enhance the overwrite cyclability. These characteristics are also responsible for their shielding effect to sulfur diffusion (Yamada et al. 1998, Zhou and Jacobs 1999). Yamada et al. (1998) reported $5 \times 10^5$ overwrite cycles with no significant modification in the optical reflectivity, signal amplitude ratio and jitter for an optical disc with GeSbTe recording layer and GeN interface layer.

To reduce thermal stress effects dielectric layers which can withstand high thermal stresses such as ZnS-SiO$_2$ can be used. To address the problem of phase separation, phase-change materials crystallizing into a single-phase should be employed because, in general, the single-phase materials (e.g. GeSbTe) show higher overwrite cyclability than the multi-phase crystallizing materials (e.g. AgInSbTe) (Borg and Schijndel 1999).
1.6.5 Data stability

The data stability or archival life stability of a phase-change memory is generally determined by the thermal stability of the recorded amorphous marks. Generally, the data is stored on an optical device by making amorphous marks in the crystalline surrounding. When such a device is subjected to high temperatures, part of the amorphous marks may spontaneously recrystallize, leading to an increase in mark size and eventually data loss. The stability of glass forming systems against crystallization is often reported in terms of the temperature interval between the glass transition temperature $T_g$ and the onset temperature for crystallization $T_c$, detected during heating a glassy sample at a steady rate. One more quantity which can be correlated with the thermal stability of glass forming systems is the activation energy, $E_A$. The activation energy for the phase change should be higher than the average thermal atomic energy ($k_B T$). This implies that $E_A >> k_B T$ which is $\sim 0.025$eV at room temperature. The activation energy can be investigated by isothermal annealing or non-isothermal annealing at constant heating rate.