TITLE: Phase-Change Media for High-Density Optical Recording

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Phase-Change Media for High-Density Optical Recording

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ABSTRACT

Rewritable optical-storage systems are quickly gaining market share in audio, video and data-storage applications. The development of new rewritable optical-storage formats with higher capacity and data rate critically depends on innovations made to the recording media incorporating so-called phase-change materials. These materials allow reversible switching between a low and high reflective state induced by laser heating. In this paper, we highlight phase-change media aspects as optical and thermal design, sputter-deposition, materials optimization, and the development of new recording strategies. Focus is on the speed race in optical recording.

INTRODUCTION

Over the past few years, the field of optical recording has evolved rapidly. Read-only disc standards (such as CD-Audio and CD-ROM) have been extended with recordable (CD-R) and rewritable (CD-RW) systems, allowing the user to create personal CDs. Simultaneously, higher-capacity systems for digital video and data applications have been developed by using shorter-wavelength lasers and stronger objective lenses. The market introduction of DVD players is proceeding even faster than the introduction of the CD some 20 years ago, and is currently being followed by rewritable versions. With the introduction of the blue-laser diode [1] and the development of high-numerical-aperture (NA) objective lenses [2], optical-storage research is currently focussing on the development of a third-generation high-capacity recording system for video and data applications. Last year, Sony and Philips presented the rewritable Digital Video Recorder (DVR) format with a user data capacity of 22.5 GB on a 120 mm disc [3], by using a blue laser (?=405 nm) and an NA=0.85 objective lens.

The technology used for these rewritable optical-storage systems is phase-change recording. The recording mechanism is based on the reversible phase transition between a crystalline and amorphous state of the recording material, induced by heating with a focussed laser beam. (Sub)micron-sized amorphous marks are written in a crystalline thin-film by using a short laser pulse to locally melt the recording layer. After switching off the laser the molten state cools down rapidly and becomes frozen in the amorphous state. Erasure of recorded marks proceeds via re-crystallization, by heating the recording material to a moderate temperature by applying an erase power level for a longer period of time.

The readout mechanism of a phase-change optical disc is similar to that of a read-only disc, as the recorded marks have a lower reflection than their crystalline surrounding. The digital information is contained in the length of the amorphous marks and the crystalline spaces in-between them. By using a recording strategy, consisting of alternating write-pulse trains with

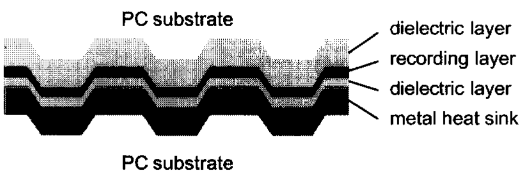

Figure 1. Typical structure of a rewritable phase-change disc, consisting of a recording stack sputter-deposited onto a pre-grooved plastic substrate.

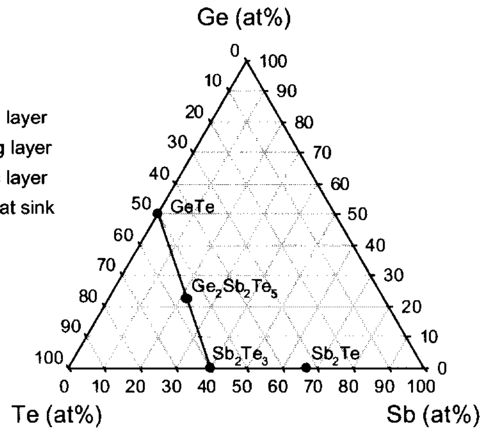

Figure 2. The Ge-Sb-Te ternary diagram. Indicated are the two classes of commonly used phase-change recording materials, *i.e.* stoichiometric compositions on the GeTe-Sb_2Te_3 tie-line and compositions near the eutectic Sb_2Te.

constant erase-power levels, it is possible to vary the length of marks and spaces and to record new data directly over previously recorded data.

In this paper, we discuss a major challenge in phase-change recording research, *i.e.* the increase of the recording speed. The maximum recording speed that can be achieved in phase-change recording is determined by the re-crystallization time of recorded amorphous marks. For high-speed recording, faster crystallizing materials as well as new write strategies to handle the increased crystallization rate have to be developed.

PHASE-CHANGE RECORDING MATERIALS

Phase-change optical-recording media generally consist of a recording stack which is sputter-deposited onto a pre-grooved polycarbonate substrate. The groove structure acts as a grating for the reflected beam, and is used for radial tracking. Address information can be included in a number of ways in the molded substrate, by superimposing a phase- or frequency-modulated sine-shaped wobble onto the groove structure, or by including read-only information in the shape of pits (headers) along the spiral-shaped tracks.

Current recording stacks comprise at least four layers. The actual recording or phase-change layer is sandwiched between dielectrics; behind this tri-layer a metal layer is present which acts as a reflector and heat sink (Figure 1). The dielectrics have various functions: They isolate the phase-change layer from the environment to prevent oxidation and segregation, they prevent the phase-change material from fluidization or evaporation during the write process, and their thickness can be used to optimize the optical contrast between the crystalline and amorphous state. Additionally, the thermal properties of the stack are strongly influenced by the dielectrics:

The thin dielectric layer between the phase-change layer and the metal mirror acts as a heat resistor, and its thickness and heat conductivity must be chosen such to combine a high cooling rate of the recording material with sufficient write-power sensitivity of the disc.

The search and development of proper recording materials is an important aspect of phase-change recording research. The suitability of the material is related to the following properties:

1. The amorphous and crystalline state have sufficient optical contrast at the recording wavelength;
2. The melting point of these materials is sufficiently low (500-1000°C), so that the material can be molten with the available laser power;
3. The crystallization of the amorphous state is sufficiently rapid. In direct-overwrite applications, the amorphous marks should be erased (re-crystallized) completely within the thermal dwell time of the laser spot, *i.e.* within a period of less than 100 ns. At the same time, for sufficient archival life of the media the amorphous phase must be stable against spontaneous crystallization at ambient and storage temperatures up to approximately 60°C. This means that the glass-transition temperature (typically 50-70% of T_{melt}) must be well above 100°C;
4. The crystalline-to-amorphous and amorphous-to-crystalline phase transitions are reversible many times (> 1000) under recording conditions.

Currently used phase-change recording materials belong to the group of semiconductor chalcogenides. The specific compositions that are being used can be divided in two classes: stoichiometric compositions on the GeTe-Sb_2Te_3 tie-line and compositions close to the eutectic Sb_2Te (Figure 2). Looking closer at the crystallization behavior of these materials, some marked differences can be observed. Figure 3 shows transmission electron microscopy (TEM) images of amorphous marks recorded in the stoichiometric $Ge_2Sb_2Te_5$ material (left panel) and a doped eutectic Sb_2Te alloy (right panel). The background of the pictures shows the crystalline state of the material obtained after initialization, i.e., after heating the as-deposited amorphous state of the material with a focussed broad array laser while rotating the disc. The crystallite size and morphology of both materials is rather different. In the stoichiometric material small spherical grains are present, whereas in the eutectic larger crystals with irregular shape can be seen. These differences can be understood by looking closer at the crystallization mechanism. In general,

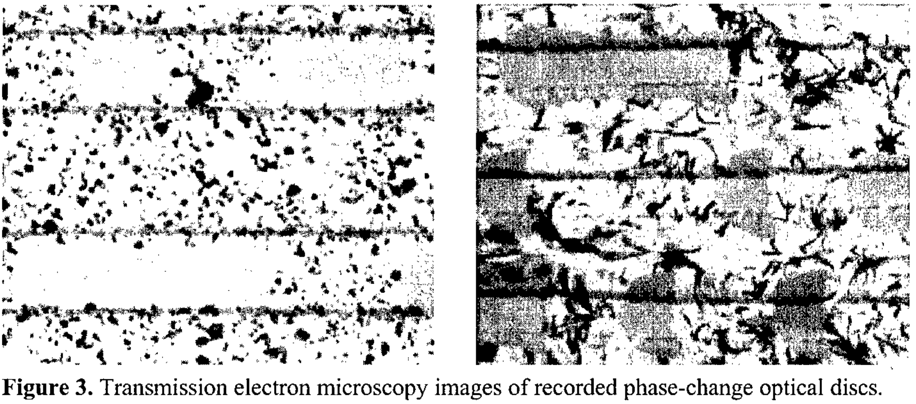

Figure 3. Transmission electron microscopy images of recorded phase-change optical discs. The left panel shows a typical image for marks recorded in the nucleation-determined stoichiometric $Ge_2Sb_2Te_5$ material, the right panel shows marks recorded in a doped eutectic Sb_2Te material.

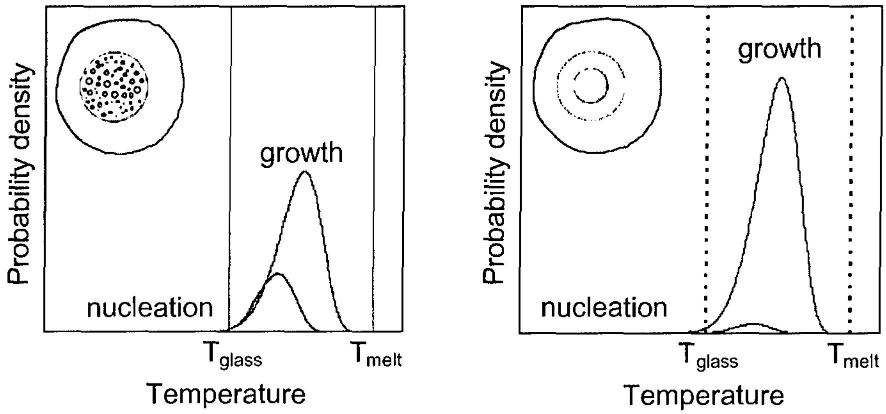

Figure 4. Schematic representation of the temperature-dependent nucleation probability and growth velocity for stoichiometric $Ge_2Sb_2Te_5$ and doped eutectic Sb_2Te compositions. In the top left corners, the resulting mechanism of mark erasure is depicted.

crystallization of the sputter-deposited amorphous state entails two processes, nucleation and growth. In the stoichiometric materials the nucleation probability is high and the growth speed is moderate. Therefore, during heating the amorphous material nuclei will be formed abundantly and grow until they coalesce. In the eutectic compositions the nucleation probability is very low while the growth speed is high. In this case, the few nuclei that are being formed during heating will grow at a faster speed, resulting in larger crystallites. Because the growth speed is relatively high, these crystallites will be irregularly shaped and contain a lot of defects.

The relative probabilities of nucleation and growth also determine the way amorphous marks are being erased (re-crystallized) under recording conditions (Figure 4). For the $Ge_2Sb_2Te_5$ and other materials with a high nucleation probability, the amorphous marks will be erased by abundant nucleation followed by moderate growth, very much like the crystallization of the sputter-deposited state ('nucleation-determined erasure'). For the doped eutectic Sb_2Te and other material with a very high growth rate, the amorphous marks will be erased by growth of the crystallites at the mark edge towards the center of the mark ('growth-determined erasure'). The nucleation probability for these materials is so low that nucleation will statistically almost never occur during the short heating cycle during recording.

HIGH-SPEED PHASE-CHANGE RECORDING

Since the introduction of CD-RW, the write speed of this system has already doubled several times, and for future higher-density rewritable-disc systems a similar speed race may be anticipated. Essential ingredients in high-speed phase-change recording are materials optimization and the development of new recording strategies. Control of the crystallization kinetics of the recording material is of crucial importance. The reduced dwell time of the spot at higher disc velocities urges for faster-crystallizing materials, while at the same time the thermal stability of the amorphous state should not be sacrificed. At current disc velocities the time for re-crystallization is typically 100 ns or less, while the amorphous marks should be stable against spontaneous crystallization for at least 30 years at room temperature. In practice, these requirements appear often contradictory, because the methods used to increase the crystallization speed of the material are often at the expense of its thermal stability.

As discussed in the previous section, two main classes of phase-change materials are currently being used for phase-change recording, nucleation-determined $Ge_2Sb_2Te_5$ and fast-growth doped-eutectic Sb_2Te. The data rates that are currently being used in rewritable DVD systems based on both types of media are similar, ranging from 11-33 Mbit/s (DVD 1X-3X speed). However, the different mark-erasure mechanism of these two types of materials has important consequences for the data rates that can be realized in phase-change recording systems with a higher bit density. The maximum write speed in direct-overwrite recording is determined by the ability to erase (re-crystallize) previously recorded amorphous marks in a single pass of the laser spot. For nucleation-determined re-crystallization, a fixed period of time is required to erase an amorphous mark. When the size of the laser spot is reduced at constant linear velocity of the disc, the dwell time of the spot will decrease. This implies that the maximum linear velocity for direct overwriting decreases with decreasing laser-spot size. Because the linear bit density increases with decreasing spot size, both trends will counterbalance. Experiments indicate that for the nucleation-determined $Ge_2Sb_2Te_5$ material the maximum write data rate is indeed essentially independent of the laser-spot size (Figure 5). For a particular growth-determined material, the maximum linear velocity that can be achieved during recording is closely related to the maximum growth speed of the recording and independent of the laser-spot size. As the linear bit density increases with decreasing laser-spot size, the maximum data rate that can be achieved with a growth-determined material increases with decreasing spot size. Experimental data have confirmed this so-called spot-size effect (Figure 5). These results indicate that doped eutectic Sb_2Te materials are becoming increasingly attractive in higher-density storage systems based on short-wavelength lasers and high-numerical-aperture lenses, and therefore these materials form

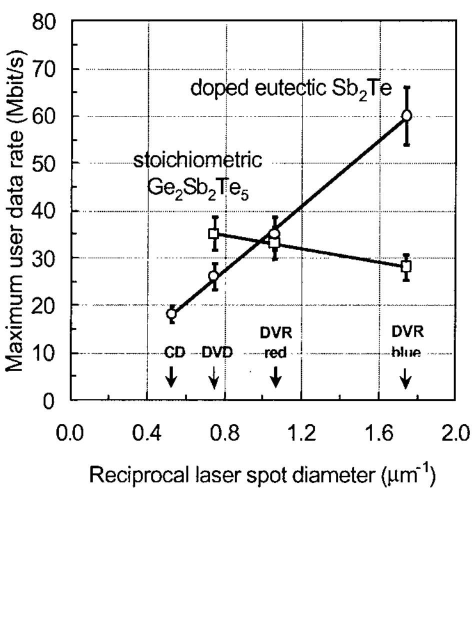

Figure 5. Maximum write data rate of the nucleation-determined $Ge_2Sb_2Te_5$ and a growth-determined doped eutectic Sb_2Te phase-change recording material, as a function of the inverse diameter of a focussed laser beam.

Figure 6. Left panel: Target used for co-sputtering, consisting of Ge, Sb and Sb_2Te_3 segments. Right panel: Magnet configuration of the rotating-magnetron cathode used for co-sputtering.

the basis for the current DVR media [4,5].

The experiments in Figure 5 were performed for the same phase-change composition and stack structure for the different laser spot sizes. In the remainder of this section we will discuss how the crystallization speed of eutectic Sb_2Te alloys can be enhanced by optimizing the composition of the alloy. For fast composition optimization we have developed a new method of co-sputtering. In this technique, a single 200-mm-diameter sputter target composed of segments of different composition is used in combination with a rotating-magnetron cathode (Figure 6) and a rotating disc-holder. While rotating the magnetron, the sputter power of the plasma can be varied from target segment to target segment. In this way, the sputter rate of the individual compounds can be controlled in a rather wide range. To achieve good uniformity of the layer thickness and composition across the entire disc, a (fixed) diaphragm with a radius-dependent aperture is mounted between the sputter target and the rotating disc. In this way, the layer's thickness and composition non-uniformity could be minimized to within 2 percent.

The eutectic Sb_2Te composition was chosen as the starting point for our experiments. The segmented target for co-sputtering consisted of Sb and Sb_2Te_3 segments of equal size, so that the Sb/Te atomic ratio could be varied easily by modulating the sputter power at both segments. Because the crystallization temperature of the eutectic is too low for practical applications, some Ge was added to the layer to improve the archival life stability of the material [6]. To this end, a small Ge-segment was included in the sputter target.

The crystallization speed of the eutectic GeSbTe alloys was studied first by using a static-tester setup [7]. In static-tester experiments, amorphous marks of different size were written by varying the write power at a fixed write-pulse length. The size of the amorphous marks was estimated from the ratio between the write power P_{write} and the power P_{melt} required to just melt the phase-change layer. Subsequently, the marks were erased by systematically changing the erase pulse power and length. In this way, the complete erasure time (CET), *i.e.* the minimum time to erase the amorphous mark, was determined [7]. The experiments were performed on actual discs, consisting of 4-layer recording stacks sputter-deposited onto a polycarbonate substrate. Figure 7 shows the measured CET values as a function of amorphous mark size, for GeSbTe alloys with an increasing Sb/Te atomic ratio and a constant Ge-concentration. For all compositions, the CET increases with the size of the amorphous mark. This is partially due to the larger distance that the mark edge has to grow, but is also caused by the decreasing temperature rise at the mark edge, due to the Airy intensity profile of the laser spot [8]. By increasing the

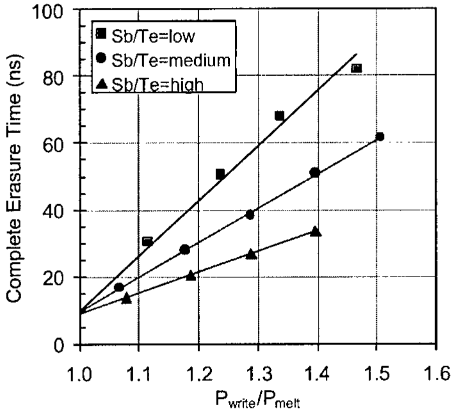

Figure 7. Complete erasure time (CET) for amorphous marks of increasing size, for eutectic GeSbTe alloys with various Sb/Te atomic ratio

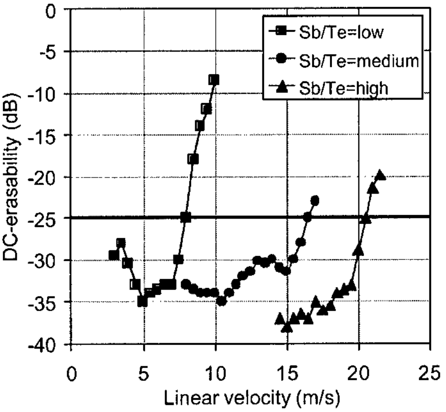

Figure 8. DC-erasability of long marks (11T pattern) as a function of the linear disc velocity, for eutectic GeSbTe with different Sb/Te atomic ratio and constant Ge concentration.

Sb/Te atomic ratio, the CET decreases significantly due to the increased growth speed of the alloy.

The phase-change composition currently used for DVD+RW is approximately equal to the slowest composition in Figure 7, and can be recorded at linear disc velocities up to 8.5 m/s (corresponding to a user-data rate of 26.5 Mbit/s). A good indication of the recording speed that can be achieved with the faster materials is given by the maximum velocity at which amorphous marks can still be erased sufficiently. Figure 8 shows DC-erasability measurements for the compositions given in Figure 7. In these experiments, data of a fixed frequency (11T, with T the channel clock period) were recorded and subsequently erased by operating the laser at DC-power at various linear velocities. The DC-power level was optimized for optimal erasability at each velocity. For proper direct overwriting a DC-erasability of at least –25 dB is required. Figure 8

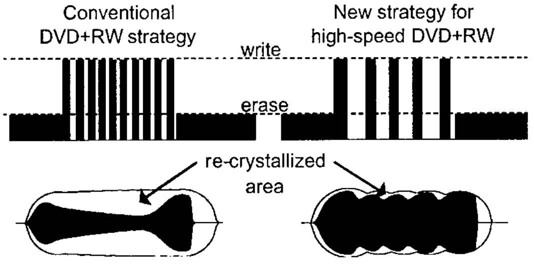

Figure 9. Conventional and new recording strategy for high-speed phase-change recording, and the (simulated) corresponding amorphous mark shapes. By reducing the number of laser pulses for writing an amorphous mark, re-crystallization during the write process can be reduced.

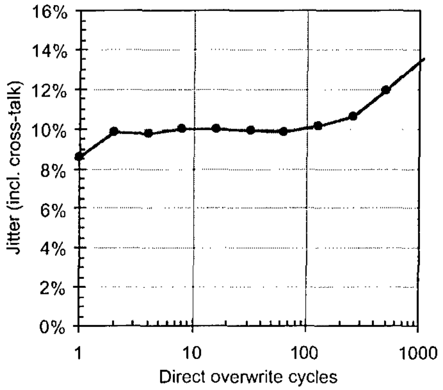

Figure 10. Timing jitter measured during direct overwriting at 53 Mbit/s (DVD 4.8X) under DVD rewritable recording conditions (λ=658nm, NA=0.65)

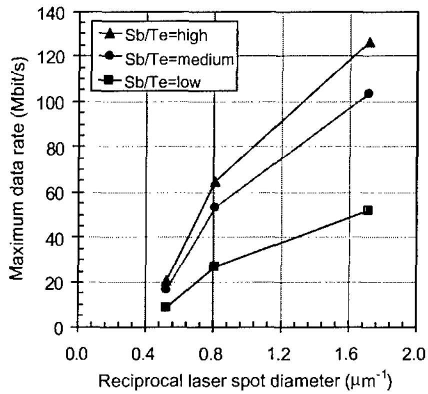

Figure 11. Extrapolation of the maximum data rate of current doped eutectic Sb_2Te alloys to the CD and DVD rewritable formats.

indicates that a linear velocity of more than 20 m/s can be achieved for the fastest GeSbTe alloys.

After optimizing the phase-change alloy composition to obtain a higher growth speed, recording experiments were performed to optimize the write strategy for high-speed recording. In a conventional recording strategy, a mark with a length of N channel bits (the channel-bit length being the shortest repetitive unit during recording) is written by applying N-1 high-power laser pulses. Each pulse results in an amorphous dot, and due to the partial overlap of the dots an amorphous mark of the correct length is recorded. However, when this conventional strategy is used in combination with fast-crystallizing materials, the temperature increase due to the next write pulses results in significant re-crystallization of the just recorded amorphous dots. This effect leads to significant reduction of the amorphous mark width, resulting in a loss of the signal amplitude. The re-crystallization phenomenon is visualized in the left panel of Figure 9, which shows the molten area and the resulting mark shape after cooling down of the disc. The mark shape was simulated by including the melt process and the temperature-dependent growth speed of the phase-change material in a thermal model of the recording process [9].

A solution to reduce the extent of re-crystallization during recording is by reducing the number of laser pulses to write an amorphous mark [10]. The right panel of Figure 9 shows a high-speed recording strategy in which the number of write pulses is only half that of a conventional strategy. Because the distance between consecutive laser pulses has doubled, the temperature increase due to consecutive pulses will be significantly reduced, reducing the extent of re-crystallization.

By increasing the Sb/Te ratio of doped eutectic Sb_2Te alloys and using high-speed recording strategies as depicted above, a significant increase of the recording speed could be realized. Figure 10 shows the jitter measured during direct overwriting under DVD rewritable conditions at a linear velocity of 16.8 m/s, corresponding to a bit rate of 53 Mbit/s (DVD 4.8X). The jitter level is close to the 9% criterion used for DVD+RW. The static tester and DC-erasability experiments indicate that materials with even higher growth speeds are still available, so that higher data rates may be realized in the near future.

It is interesting to extrapolate the data rates obtained under DVD recording conditions (λ=658 nm, NA=0.65) to the CD-RW system (λ=780 nm, NA=0.50) and the high-density DVR system (λ=405 nm, NA=0.85). As discussed before, the maximum *linear* velocity that can be achieved is more or less independent of the laser spot size for growth-determined re-crystallization. This means that the data rates that can be achieved under CD-RW and DVR conditions can be estimated by correcting for the linear bit density and the efficiency of these formats relative to the DVD+RW format. Figure 11 shows such an extrapolation for the materials discussed previously. The data rates for the CD-RW system are much lower than would be expected on the basis of the laser-spot size, due to the relatively low linear density and efficiency of this format. For the DVR system data rates of over 100 Mbit/s are predicted for these doped Sb_2Te alloys. In this context, it is interesting to note that we have already reported a data rate of 80 Mbit/s under DVR-blue recording conditions [5].

CONCLUSIONS

The field of optical recording is evolving rapidly, showing an increasing market share for rewritable disc systems based on phase-change recording. The recording mechanism is based on writing (sub)micron-sized amorphous marks in a crystalline recording layer by heating with the focussed laser beam. The recorded marks can be erased by re-crystallization. The recorded data can be read from the reflectivity difference between both states, similarly as in read-only discs. The popularity of phase-change technology can therefore partially be explained by the playback compatibility of the rewritable media on read-only drives.

Current phase-change media are generally based on either of two material classes: stoichiometric compositions on the $GeTe$-Sb_2Te_3 tie-line, in particular $Ge_2Sb_2Te_5$, or compositions close to the eutectic Sb_2Te. An important difference between both materials is the erase mechanism of recorded marks: In the stoichiometric compositions re-crystallization is dominated by nucleation, whereas in the doped eutectic Sb_2Te re-crystallization is determined by growth of the mark edge.

The maximum write data rate in phase-change recording is determined by the time required to erase previously written amorphous marks. For nucleation-determined erasure, the data rate that can be achieved is independent of the laser-spot size. For growth-determined erasure, a significant increase of the write speed can be realized by using a smaller laser spot. This implies that materials with growth-determined crystallization such as doped Sb_2Te become increasingly attractive at higher recording densities.

By using a new method of co-sputtering, the composition of the eutectic Sb_2Te was varied to investigate its feasibility for recording at higher write speeds. By increasing the Sb/Te atomic ratio of the alloy, the growth speed could be increased significantly, whereas the addition of some Ge improved the thermal stability of the amorphous state. The higher growth speed leads to increased re-crystallization during the write process. To reduce this effect, a new recording strategy with a reduced number of write pulses has been developed. In this way, data transfer rates of up to 53 Mbit/s have been achieved for rewritable DVD+RW media. Scaling this value to the higher density of the rewritable DVR system, data rates of higher than 100 Mbit/s will be realized by using a blue-laser diode and a higher-numerical aperture lens.

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REFERENCES

1) S. Nakamura and S. Fasol: *The Blue Diode Laser* (Springer-Verlag, Berlin, 1997).
2) K. Yamamoto, K. Osato, I. Ichimura, F. Maeda and T. Watanabe, *Jpn. J. Appl. Phys.* **36**, 456 (1997).
3) K. Schep, B. Stek, R. van Woudenberg, M. Blüm, S. Kobayashi, T. Narahara, T. Yamagami and H. Ogawa, to be published in *Jpn. J. Appl. Phys.* **40** (2001).
4) H.J. Borg. P.W.M. Blom, B.A.J. Jacobs, B. Tieke, A.E. Wilson, I.P.D. Ubbens and G.F. Zhou, Optical Data Storage/International Symposium on Optical Memories 1999, *Proceedings SPIE* **3864**, 191 (1999).
5) H.J. Borg, M. van Schijndel, J.C.N. Rijpers, M.H.R. Lankhorst, G.F. Zhou, M.J. Dekker I.P.D. Ubbens and M. Kuijper, *Jpn. J. Appl. Phys.* **40**, 1592 (2001).
6) M.H.R. Lankhorst and H.J. Borg, this symposium, to be published in MRS Proceedings.
7) J.H. Coombs, A.P.J.M. Jongenelis, W. van Es-Spiekman and B.A.J. Jacobs, *J. Appl. Phys.* **78**, 4906 (1995).
8) G.F. Zhou, H.J. Borg, J.C.N. Rijpers, M.H.R. Lankhorst and J.J.L. Horikx, Optical Data Storage 2000, *Proceedings SPIE*, **4090**, 108 (2000).
9) E. R. Meinders, H.J. Borg, M.H.R. Lankhorst, J. Hellmig and A.V. Mijiritskii, Optical Data Storage 2001, to be published in *Proceedings SPIE*.
10) M. Horie, N. Nobukuni, K. Kiyono and T. Ohno, Optical Data Storage 2000, *Proceedings SPIE* **4090**, 135 (2000).