SYMPOSIUM HH

HH: Phase Change and Nonmagnetic Materials for Data Storage

December 1 - 4, 2003

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TUTORIAL

FT HH: Phase-Change Data Storage
Monday, December 1, 2003
9:00 AM - 4:30 PM
Hampton (Sheraton)

The tutorial will give an overview of phase-change data storage. The session will begin with an introduction covering the history of phase change and its position in the area of data storage. After the introduction, major data-storage technologies utilizing phase-change principles will be considered. In this section, background information, recording techniques, short systems description, storage-media design, and materials requirements, as well as the recent developments and trends, will be addressed. The technological section of the tutorial will be followed by a closer look at the physics and chemistry of phase-change materials. In particular, optical, thermal, mechanical, and electronic properties will be considered. Both theoretical understanding and experimental results will be discussed. The tutorial is primarily aimed at scientists doing materials research who would like to learn more about both phase-change materials and their current and future technological applications.

Instructors:
Stanford R. Ovshinsky, Energy Conversion Devices, Inc.
Motoyasu Terao, Hitachi Central Research Laboratory
Stephen J. Hudgens, Ovonyx, Inc.
Masud Mansuripur, University of Arizona
Matthias Wuttig, Physics Institute of Aachen RWTH

SESSION HH1: Phase Change Electronic Memories I
Chairs: Matsud Mansuripur and Takeo Ohta
Tuesday Morning, December 2, 2003
Hampton (Sheraton)

8:30 AM *HH1.1
Innovation Providing New Multiple Functions in Phase-Change Materials to Achieve Cognitive Computing.
Stanford R. Ovshinsky, Energy Conversion Devices, Inc., Rochester Hills, Michigan.

The Ovonic^{Ch} Cognitive Computer is a technology that fulfills the long-awaited goal of achieving intelligent computing. While a single device (or, in some cases, two devices) of subnanometer size is able to have many multiple functions, such as the demonstration of addition, subtraction, multiplication and division, and the standard binary activity of any computer, it also can do nonbinary processing, modular arithmetic and encryption, as well as factoring. It has the adaptability/plasticity of a biological neurosynaptic cell and can be used as a densely interconnected network of proprietary Ovonic^{Ch} cognitive device. The same device offers multifunctionality. Like biological neurons, the device is capable of synaptic function, such as receiving and weighting multiple inputs that result in threshold activation, an operational mode in which it accumulates input energy signals without responding until the total accumulated energy reaches a threshold level. Once the threshold is reached, the device undergoes an abrupt transformation from a high resistance state to a low resistance state in a process that mimics the firing of a biological neuron in response to synaptic signals. The active chalcogenide material of the Ovonic^{Ch} devices and the Ovonic^{Ch} Cognitive Computer can be deposited by a low-cost, production thin-film technology. They can also be integrated and embedded, that is, hybridized with conventional silicon circuitry. We will describe the device and show data that demonstrate that new types of computers, semiconductors and production machinery are made possible by this unique multifunctional device which operates in a nano regime and, in fact, has some features that are analogous to the much-sought after quantum computer.

9:00 AM *HH1.2
Understanding the Electro-thermal and Phase-transformation Processes in Phase-change Materials for Data Storage Applications. C. David Wright, Marilyn Armand, Mustafa Aziz, Semih Senkader and Wanhua Yu; University of Exeter, Exeter, United Kingdom.

The application of phase-change alloys, for example GeSbTe and AgInSbTe, to optical data storage is now quite well established, with rewritable versions of the CD and DVD formats already on the market. Of course technology does not stand still, and development of even higher capacity phase-change based optical disks, such as the Blue-Ray system, is already underway. Phase-change materials also have many properties that make them suitable for electrical type memories; in particular the electrical resistivity varies by 3 or 4 orders of magnitude between the amorphous and crystalline states. This effect is being utilized in new solid state devices, the so-called PC-RAM (phase-change random access memory) chips that may offer a future alternative to conventional CMOS based memories. Yet another possibility is the use of phase-change materials in a scanning probe based storage system. The feasibility of a high density, high data-rate, scanned probe memory has already been demonstrated by IBM Zurich group via their Millipede system, where a 2-D array of around 1000 heated AFM-type tips write to and read from a polymer medium with bit sizes down to 50nm and less. The IBM polymer medium is essentially a write-once material, and it is natural to ask whether or not a similar concept of scanning probe based storage can be extended to known rewritable materials - in particular to phase-change media. Thus, it is clear that phase-change materials may find use in many different memory architectures, and it is desirable to have a thorough understanding of the electrical, thermal and kinetic processes that may be involved in such applications. In this paper we present results of a theoretical and computational study of such processes, focusing in particular on the application areas of scanned probe storage and solid state electrical memories.

9:30 AM *HH1.3
Conductive Transparent Probes And Their Applications To High-Density Phase-Change Data Storage By Using Current Injection. Tooru Murashita, Photonics Labs., NTT, Atsugi, Kanagawa, Japan.

High-density terabits/inch2 data storage requires nanometer-sized marks. With the goal of producing such storage, we are studying a method in which nanometer-sized marks are recorded on GeSbTe phase-change media by current beams from sharpened probes. Current beams can inject heating power with lower transmission losses into nanometer-sized regions that are smaller than the refraction limit of light. Moreover, the conductivity of amorphous GeSbTe is more than two orders lager than that of crystalline GeSbTe. Therefore, current beams are advantageous for high-density data storage with nanometer-sized marks. We have developed a simulator for phase change processes in which joule heats and Jhonson-Mehl-Avrami equation are used. We have simulated temperatures of Ge2Sb2Te5 on a metal electrode in space and time domains as a function of current injection conditions. The results clarify that a small amorphous mark about 20 nm in radius can be made in a crystalline Ge2Sb2Te5 region by injecting a 20-ns-long 9.5-?W probe current pulse. The probes have to supply high current densities and bias voltages to produce phase change. The probes must therefore be robust for these severe conditions. A conductive transparent (CT) probe we have developed for precise characterization of optical and electronic properties with nanometer-level spatial resolution is applicable for this purpose. The CT probes consist of a transparent electrode coated on an optical fiber tapered to a point with a nanometer-level radius. The probe current derived from the simulation can be injected by using the CT probes with a metal oxide electrode. The CT probe with the transparent electrode also has unique performance in that it can inject current in a nanometer-sized region and simultaneously illuminate on the same local region. This leads to a new method of light-assisted current phase-change recording by using the transparent electrode.

10:30 AM HH1.4
Amorphous-to-fcc Transition in GeSbTe Thin Films.
Stefania Privitera[1], Corrado Bongiorno[2], Emanuele Rimini[1,2], Corrado Spinella[2], Romina Zonca[3], Agostino Pirovano[3,4] and Roberto Bez[3]; [1]Dipartimento di Fisica e Astronomia, University of Catania, Catania, Italy; [2]Istituto di Microelettronica e Microsistemi (IMM), CNR, Catania, Italy; [3]Central R&D, STMicroelectronics, Agrate Brianza (Mi), Italy; [4]Dipartimento di elettronica e informazione, Politecnico di Milano, Milano, Italy.

The electrical properties of GeSbTe films and their compositional dependence are extremely important for application of phase change materials for nonvolatile random access memories (PCRAM). For these applications it is very important to understand and control the nucleation and growth processes, which might be limiting factors for the scalability. Therefore, a detailed thermodynamical description of the driving force for the amorphous-to-polycrystal transformation and of the nucleation barrier energy is required. With this aim we studied the kinetics of nucleation and growth of *fcc* grains in GeSbTe amorphous thin films with composition around $Ge_2Sb_2Te_5$, under isothermal anneals in the temperature range 130-190°C. The effect of annealing temperature and time on the structure and the electrical properties of non-stoichiometric compositions have been compared with those of the stoichiometric $Ge_2Sb_2Te_5$ through X ray diffraction analysis, transmission electron microscopy and in situ electrical measurements. An activation energy of 2.7 ± 0.2 eV has been obtained for the amorphous-to-fcc transition in $Ge_2Sb_2Te_5$. Phase separation has been observed in samples with excess of Ge, in which

part of the material does not convert into the crystalline structure under annealing at temperatures below 170°C. Moreover, in order to separate the contribution of nucleation and growth, the two processes which govern the amorphous-to-crystal transition, X ray diffraction and electrical measurements, which provide only average volume information as a function of time, have been coupled with in situ transmission electron microscopy, which allows to measure also the grain density and size during the transition. By using this technique, the nucleation and growth parameters have been determined and their dependence on the temperature has been evaluated.

10:45 AM HH1.5
Study of the Structural Transformation of GeSbTe Induced by Current Pulses in Phase Change Memory. Rong Zhao, Tow Chong Chong, Hao Meng, Pik Kee Tan, Kai Jun Yi, Ke Bin Li, Yi Hong Wu and Lu Ping Shi; Data Storage Institute, A*Star, Singapore, Singapore.

In this paper, we investigated the structural transformation of GeSbTe thin films induced by current pulses in phase change electronic memory by Raman spectroscopy and transmission electron microscopy (TEM). The phase structures were compared to those of the thin films crystallized by thermal and laser. It was found that the Raman spectra for the thin films crystallized by current pulses were different from those by thermal and laser annealing, and the Raman spectra were dependent on the different current pulse width. Variations in the structural transformation due to composition, temperature, laser and current power were studied. Meanwhile the electrical properties for the GeSbTe thin films due to the structural changes by current pulse, thermal and laser were measured. In order to design the phase change electronic memory with better performance, it is important to understand the phase transformation inside the memory device. We employed TEM to observe the phase transformation of the GeSbTe alloy inside the memory active pore. Memories at different Set/Reset states, switched by different current pulse width and switching cycles was analyzed by TEM. The possible mechanism involved in the current induced crystallization was discussed. Based on the above experimental results, a new recording stack was developed for electronic memory device in order to reduce the current power and increase the Set/Reset switching speed. The Set/Reset current was greatly reduced at short pulse width (< 10 ns). The Set/Reset cycles and stability were also improved. More data and the discussion will be presented in the conference.

11:00 AM HH1.6
Electronic Phase Change Characteristics of GeSbTe-Based Chalcogenide Alloys at the Memory Cell with 50 and 70 nm Contact Holes. Dong-ho Ahn[1], D.H. Kang[1], H.S. Kwon[1], M.H. Kwon[1], T.Y. Lee[1], B. Cheong[2], K.S. Lee[2], D.H. Kim[2], T.S. Lee[2], W.M. Kim[2] and K.B. Kim[1]; [1]School of Materials Science and Engeneering, Seoul National University, Seoul, South Korea; [2]Thin Film Materials Research Center, Korea Institute of Science and Technology, Seoul, South Korea.

From a feasible read-mostly memory device appearing in 1970 [1], phase change random access memory (PCRAM) based on chalcogenide semiconductors has come near to the practical use as a high performance non-volatile memory. Little has been known to date, however, with regard to the scalability of the memory such as the operating current scaling for high density memory application and the reliability of reversible phase change between a crystalline (SET) and an amorphous (RESET) state in an extremely small contact area [2]. Herein, our recent study is presented regarding the electrical switching behaviors of GeSbTe-based alloys of three different compositions such as $Ge_2Sb_2Te_5$, $Ge_1Sb_2Te_4$, and $(Ge_1Sb_2Te_4)_{0.9}(Sn_1Bi_2Te_4)_{0.1}$ in the off-set structure memory cell with a contact diameter of 50nm and 70 nm, respectively. By the sequence as shown, these alloys are known to have progressively the decreasing melting temperatures and activation energies for crystallization as well [3]. Memory cells with the off-set structure are made for each alloy by the procedure as follows. The GeSbTe-based alloys and electrodes were deposited by a magnetron sputtering and the contact holes were fabricated by an e-beam lithography followed by reactive ion etching (RIE) dry etch. For three kinds of memory cells, the electrical measurements of dc steady-state and transient on-off test were carried out. An experimental finding was made, for the first time, that the reversible phase switching of GeSbTe-based alloys is possible in a contact hole as small as 50 nm size. The differences in the resistance due to phase changes between SET and RESET state for each alloy are as large as two orders of magnitude. These differences are sufficient to identify the memory state. Different switching parameters for the three alloys such as the discerned values of V_{th}, I_{set}, R_{set} and R_{reset} are summarized as shown in Table 1. It is believed that these results are attributed to the differences in phase change characteristics and in the electronic conduction behavior among the three alloys. Detailed results and mechanisms will be addressed. [1] R.G. Neale *etal.*, Amorphous semiconductor, p. 56, 1970 [2] R. Neale, Electronic Engineering, p. 67, 2001 [3] Tae-Yon Lee *etal.*, Appl. Phys. Lett., Vol. 80. No. 18, p. 3313, 2002 and references therein. Table.1 Critical parameters of memory cell with 50 and 70 nm contact holes.

11:15 AM HH1.7
Effect of thermal treatments on the Ti-Ge2Sb2Ge5 system. Romina Zonca[1], Alberto Modelli[1], Alessandro Giussani[1], Stefano Alberici[1], Giuseppe Pavia[1] and Enrico Varesi[2]; [1]Central R&D, STMicroelectronics, Agrate Brianza, Italy; [2]Laboratory, MDM-INFM, Agrate Brianza, Italy.

For both phase change optical data storage and phase change memory, also known as OUM, a key parameter in terms of performance and reliability of the device itself is the stoichiomentry of the chalcogenide material and its stability during cycling. In this framework, the study of the interactions between the chalcogenide media and the surrounding materials in the device is of primary importance to control the effect of thermal budgets connected to either the fabrication of the storage element or to the switching during cycling. In this work we have studied the effect of a thermal treatment on a layered structure of Ge2Sb2Te5 and Ti films. The modification of the as deposited film respect to the annealed one has been measured by means of SEM and TEM cross sections while the variation in composition has been evaluated through AES, ToF-SIMS depth profiles. A different stack consisting of Ti-Ge2Sb2Te5-Ti films have been also prepared and analyzed to verify possible measurement artifacts related to different sputtering yield while profiling. XRD analyses have been performed to evaluate new metal phases formed after annealing. The experiment showed that Ge2Sb2Te5 is not stable with respect to Ti-Te interaction: after the annealing at 400 C a Ti-Te compound, likely TiTe2, is formed depleting Te in the Ge2Sb2Te5 layer.

11:30 AM HH1.8
Thermal analysis of nonvolatile and non rotation phase change memory cell. Luping Shi, T.C. Chong, J.M. Li and M.Q Mou; Data storage institute, Singapore, Singapore.

This paper focuses on thermal analysis of Chalcogenide Random Access Memory (C-RAM), also known as Ovonic Unified Memory (OUM). In C-RAM technology, a short programming electrical pulse is used to switch the memory cell between the amorphous and crystalline states that may denote zero and one, respectively. In C-RAM, data storage implemented by a thermally induced phase-change between the amorphous and crystalline states in a chalcogenide phase change thin film. Thus, it is important to investigate the thermal influence of factors such as cell structure, electric peak power and pulse length on the performance of the C-RAM. Three-dimensional thermal finite-element method (FEM) is applied to analyze the C-RAM cell. The thermal effect generated by the incident electric pulse is mainly addressed. In this simulation, TiW and TiWN are used as electrodes, ZnS-SiO2 as an isolation material and GeSbTe as a phase change material. Performance of the cell as a result of electrical parameters and geometrical variations are quantified. The thermal effect of different electrical pulse shape is also investigated. Current flow in the memory cells is calculated and illustrated. The heat generation source was calculated based on the current flow calculation. Temperature profiles, temperature change over time, heating rate, cooling rate and heat flow characteristics are analyzed. From the simulation results, it can be concluded that the thermal performance of C-RAM cell is strongly depend on the cell structure, especially the cell size. The results of the heat diffusing to the neighbor cell give us the information that how small we can assemble the memory array. The heat generated in the memory cell diffuses not only to neighbor cell but also to the button side, which may affect the performance of the CMOS. The simulation results are important for us to control the heat diffusing towards to the button.

11:45 AM HH1.9
Reversible Optical Recording on Epitaxial Indium Selenide Phase-Change Media. Alison Chaiken[1], Gary A Gibson[1], Chris Nauka[1], C.C. Yang[1], Bao S. Yeh[2], Robert Bicknell-Tassius[2], John Chen[2], Hung Liao[2], Mani Sivaramakrishnan[2], Darin D. Lindig[3], Jacek B Jasinski[4] and Zusana Liliental-Weber[4]; [1]Advanced Storage Dept., Hewlett-Packard Labs, Palo Alto, California; [2]Imaging and Printing Group, Hewlett-Packard, Corvallis, Oregon; [3]Imaging and Printing Group, Hewlett-Packard, Boise, Idaho; [4]Materials Science Division, Lawrence Berkeley National Lab, Berkeley, California.

Media noise due to grain boundaries becomes an increasingly difficult problem as the bit density of optical recording increases. One approach to controlling noise is to use epitaxial media films with a minimum number of defects at small length scales. We describe optical recording studies on InSe/GaSe/Si (111) films. The growths of InSe/GaSe[1] and of GaSe/Si(111)[2] have been reported previously. InSe has unusual properties for a phase-change material: a hexagonal layered structure, anisotropic thermal transport parameters and a

peritectic decomposition upon melting. Amorphous bits as small as 100 nm in diameter have been made using short laser pulses (30 ns) that are less than the thermal equilibration time of the stack. The amorphization has been confirmed using techniques such as reflectivity, optical beam-induced current (OBIC), atomic force microscopy and transmission electron microscopy. Recrystallization of the amorphous regions has been accomplished using lower-power millisecond laser pulses. Up to 100 write-erase cycles with partial restoration of reflectivity and OBIC have been achieved. Electron microscopy studies suggest that the recrystallization starts at the edge of the amorphous region and propagates into the center. The ability to cycle the material has been limited by damage to the surface, which is not clad with the thick dielectric layers used in CD/DVD products. Possible improvements with respect to the recrystallization time and media robustness will be discussed in light of published studies of 10^6 cycles of direct overwrite recording on off-stoichiometric polycrystalline In-Se-Tl films.[3] [1] N. Nakayama, T. Kuramachi, T. Tanbo, H. Ueba, and C. Tatsuyama, Surf. Sci. 244, 58 (1991). [2] J.E. Palmer, T. Saitoh, T. Yodo and M. Tamura, J. Cryst. Growth 147, 283 (1995). [3] T. Nishida, M. Terao, Y. Miyauchi, S. Horigome, T. Kaku and N. Ohta, Appl. Phys. Lett. 50, 667 (1987).

SESSION HH2: Phase Change Electronic Memories II
Chairs: Kristin A. M. Scott and Junji Tominaga
Tuesday Afternoon, December 2, 2003
Hampton (Sheraton)

1:30 PM *HH2.1
Characteristics of OUM Phase Change Materials and Devices for High Density Nonvolatile Commodity and Embedded Memory Applications. Tyler Lowrey[1], Chuck Dennison[1], Steve Hudgens[1] and Wally Czubatyj[2]; [1]Ovonyx, Inc., Santa Clara, California; [2]Ovonyx, Inc., Rochester Hills, Michigan.

Phase change memory devices were originally reported by Stan Ovshinsky in 1968. A 256 bit phase-change memory array based on chalcogenide materials was reported by R.G. Neale, D.L. Nelson and Gordon E. Moore of Energy Conversion Devices and Intel in 1970. Recent advances in phase change materials, memory device designs, and process technology have resulted in dramatic advances in phase change device performance, and a new memory device, called Ovonic Unified Memory (OUM) has been developed. This paper will discuss various device and materials characteristics of OUM phase change memory materials of interest in application for non-volatile high-density memories. These materials are generally Te chalcogenide based, exploiting the congruent crystallization of the FCC phase and the associated dramatic reduction in resistivity that results from crystallization from the quenched vitreous amorphous state. Data storage is accomplished by a phase change between amorphous and polycrystalline states which is a thermally activated, rapid, reversible structural change in the phase change film. While rewriteable DVD disks employ laser heat to produce the phase change, OUM technology uses a short electrical current pulse to achieve the amorphous state (high resistance RESET state), and a lower amplitude, wider current pulse to convert the material to the polycrystalline state (lower resistance SET state). Joule heating to stimulate phase transitions is derived from both device IV and electrode I2R power dissipation. The device thermal environment dictates the power and energy required for memory state programming. A review of the device structure, characterization data, device performance, and reliability as well as device modeling results will be presented in the full paper. Characteristics of key material and device performance metrics such as crystallization and amorphization programming speed will be reviewed. Programming algorithms will be reviewed for optimizing operating margin for high-density applications. Data retention characteristics will be reviewed along with means for accelerated statistical evaluation. The device structure, aspects of fabrication, and characterization of the memory element will be reviewed. Potential high-density memory array data disturb issues will be identified and their impact on performance and scalability will be discussed. Scaling attributes and issues will be reviewed.

2:00 PM *HH2.2
Fast-Switching and long Data-Retention Materials For Phase-Change Memory. Martijn Lankhorst, R.A.M. Wolters, L. van Pieterson, W.S.M. Ketelaars, J.T. van Hulle, F.C. van den Heuvel, J.P. van Zijl and J.H.J. Roosen; Philips Research, Eindhoven, Netherlands.

Recently, there is growing interest in novel non-volatile memory technologies with better performance and scaling than the existing flash-type memories. Phase-Change RAM (PCRAM) also called Ovonic Unified Memory (OUM) is one of the promising options because it has good switching characteristics (fast <50ns, low voltage <3V, high ON/OFF ratio ~10^2, long endurance > 10^9) for a relatively low cost per bit. In PCRAM, programming of bits is accomplished by a Joule heating induced phase-change between a high-resistive amorphous and a low-resistive crystalline state in a phase-change material. To switch to the high-resistive state, the short RESET-current pulse melts the material, after which the material is quenched into the amorphous state. To convert the material back into the low-resistive and stable polycrystalline state, the somewhat longer SET-current pulse heats the material to above its crystallization temperature. So far, phase-change material compositions along the GeTe-Sb_2Te_3 tie-line (GST) such as $Ge_2Sb_2Te_5$ are generally reported to be used in PCRAM. There are, however, other promising material candidates for PCRAM with properties different from GST. In this paper we will report on our research on 2 other material classes that in comparison to GST have faster crystallisation speed and better stability of the amorphous state. The faster crystallisation speed allows for short SET-pulses (<20 ns) to be used, while the better amorphous stability leads to improved data retention (10 years above 200^0C). The better amorphous stability also decreases write disturb problems, i.e. spontaneous crystallisation of amorphous cells during programming of the adjacent cells. As such these materials allow for higher density packaging of cells, which is crucial for stand-alone memories. We will further report on important electrical properties of these materials for PCRAM application like resistivity and threshold voltage. Switching experiments were done on single cell devices. Low switching currents were obtained by making cells with submicron dimensions using E-beam structuring and/or using sidewall-spacers.

2:30 PM *HH2.3
Investigations Of Nitrogen Doped $Ge_2Sb_2Te_5$ Thin Film For Phase Change Random Access Memory. Soon Oh Park[1], J. H. Park[1], J. H. Yi[4], Y. H. Ha[1], B. J. Kuh[1], H. Horii[1], Y. N. Hwang[2], S. H. Lee[2], S. J. Ahn[2], Y. T. Kim[3], K. H. Lee[3], U-In Chung[1] and J. T. Moon[1]; [1]Process Development Team, Samsung Electronics Co., Ltd, Yongin-Si, Kyungki-Do, South Korea; [2]Advanced Technology Development Team, Samsung Electronics Co., Ltd, Yongin-Si, Kyungki-Do, South Korea; [3]CAE Team, Samsung Electronics Co., Ltd, Yongin-Si, Kyungki-Do, South Korea; [4]Advanced Process Development PT, Samsung Electronics Co., Ltd, Yongin-Si, Kyungki-Do, South Korea.

Phase Change Random Access Memory[PRAM] is one of the candidates for next generation memory due to its non-volitality, high speed, high density and compatibility with Si-based semiconductor process. $Ge_2Sb_2Te_5$ [GST] thin film, an active layer in this device, is utilized because it has the well-known property of rapid crystallization without phase separation in erasable compact discs industry. We investigated nitrogen doped GST to reduce operation current, which is one of key issues in present PRAM development. A 100nm thick GST film was prepared with DC sputtering system for this experiment. XRD, TEM, SEM and four-point probe techniques are used to analyze the physical and electrical properties of this film. We found that nitrogen-doped GST maintain fcc structure up to 400°, while undoped GST was mixed-phase of fcc and hcp. This stable phase of the Nitrogen doped GST film retained its high resistivity even after 400° annealing. In addition, crystallization temperature was increased from 120° to 185° with nitrogen doping. To find out the effect of Nitrogen doping, we fabricated extremely small contact size(~80nm) between GST cell and bottom contact with 0.24 mm design rule CMOS. The operation current was successfully reduced from 1.5mA to 0.6mA by controlling the concentration of nitrogen during the film deposition. This reduction is attributed to the decreasing of the grain size from 100nm to 25nm, which decreases the thermal conductivity and the electron mobility of the GST film.

3:15 PM HH2.4
Applications of High Throughput Methods to the Development of Materials for Non-Magnetic Storage. C. Eric Ramberg, Youqi Wang, Qun Fan, Eriko McDermott, Jason Wang, Kirk Kenyon and Sum Nguyen; Symyx Technologies, Santa Clara, California.

High throughput, thin film synthesis methods (e.g. Sputtering, Pulsed Laser Deposition, Electron Beam Evaporation) have been used to make intermetallics, nitrides, chalcogenides, pnictides, and other compositions, with microstructures ranging from epitaxial to multilayer to amorphous. Optical, electronic, crystallographic, and other properties have been measured using a diverse range of methods. This talk focuses on the use of isothermal annealing experiments, combined with post-situ X-ray diffraction, to examine the phase stability of metallic and semiconducting materials. These data are complemented by in-situ measurements of properties vs. temperature.

3:30 PM HH2.5
Electric Local Surface Modification of ECR Sputtered Carbon Film and Its Application to High Density Data Storage. Shigeki Tsuchitani[1], Masanori Isozaki[1], Reizo Kaneko[1], Ichiro Tanaka[2] and Shigeru Hirono[3]; [1]Department of Opto-Mechatronics,

Wakayama University, Wakayama-shi, Wakayama, Japan; [2]Department of Material Science and Chemistry, Wakayama University, Wakayama-shi, Wakayama, Japan; [3]NTT Afty Corporation, Musashino-shi, Tokyo, Japan.

Point recording, which forms small data bits with a sharp recording tip, is an effective method for ultra high density data storage. We propose a point recording which uses an ECR sputtered carbon film as a recording material and modifies the carbon surface electrically by a conductive tip. ECR sputtered carbon film has high hardness and large electrical conductivity because of its three dimensional sp2 network structure[1]. Therefore, it is suitable for an electrical point recording and does not need a wear resistive protective overcoat as usual magnetic recording media. The carbon film was deposited by ECR sputtering on a silicon substrate covered by a thermal oxide layer. The recording experiments on the carbon film were carried out by a contact AFM with a gold coated conductive tip. The electrical resistance of the carbon film was decreased by applying a voltage (recording voltage) between the film and the tip. The fractional change in the resistance was independent of the polarity of the voltage, and increased with the magnitude of the voltage up to 2V and was almost constant above 2V. I/V curves measured by contacting the AFM tip with the carbon surface were nonlinear and symmetry with respect to the origin before the application of the recording voltage. After the recording, the linearity of the I/V curves increased, i.e. they approached ohmic characteristics. From these results, the decrease in the resistance of the ECR sputtered carbon film by the application of the recording voltage is thought to be due to graphitization caused by the heating of the contact portion of the carbon film with the AFM tip. Small data bits with size of 80nm to 100nm were formed by applying a pulse row as a recording voltage. [1] S. Hirono, S. Umemura, M. Tomita, and R. Kaneko, Appl. Phys. Lett. 80, 425 (2002)

3:45 PM HH2.6
An Electron-Beam Addressed Phase-Change Recording Medium. Gary Gibson[1], Alison Chaiken[1], K Nauka[1], Chung-Ching Yang[1], Robert Davidson[1], Anthony Holden[1], D D Lindig[1], Robert Bicknell-Tassius[2], John Chen[2], Hung Liao[2], David Neiman[2], David Schut[2], S Subramanian[2], Bao S Yeh[2], Jacek Jasinski[3] and Zuzanna Liliental-Weber[3]; [1]Advanced Storage Department, Hewlett-Packard Laboratories, Palo Alto, California; [2]Imaging and Printing Group, Hewlett-Packard, Corvallis, Oregon; [3]Lawrence Berkeley National Lab, Berkeley, California.

We describe the development of an ultra-high density, phase-change storage medium that can be written and read using electron beams. This storage medium includes an epitaxial stack of n-InSe/p-GaSe/p-Si(111) that forms a pn-junction diode. Amorphous regions are reversibly created in the InSe layer via appropriate heating pulses from either a laser or electron beam. These 'bits' are detected while scanning the laser or electron beam over the medium at a power density insufficient to cause recrystallization. The electron-hole pairs generated by this read beam are separated by a combination of built-in and applied electric fields in the diode, which is reversed biased. The resulting increase in diode current constitutes the readout signal. The amplitude of this induced current depends on the local minority carrier collection efficiency, which is much lower in the neighborhood of an amorphous bit. The set of material properties needed to make this device work is quite restrictive. In addition to being phase cyclable, the phase-change layers must form a low-leakage, rectifying junction that has a high minority carrier collection efficiency in the crystalline state. The layered compounds InSe and GaSe show great promise for providing this functionality. Due to highly anisotropic bonding, their surfaces have relatively few problems with defects such as dangling bonds that cause recombination. This allows us to create low-leakage diodes with a collection efficiency of 5% for carriers generated at the surface of crystalline regions by a 700 eV electron beam. Carrier collection is negligible when the same beam is incident on 25 nm deep amorphous bits. Data on the signal contrast as a function of electron beam energy, bit size, and number of write/erase cycles (contrast up to 9 X beam current at 700 eV), as well as measurements of media noise ($\sim$ 25 dB) and the frequency response of our diodes ($\sim$ 1MHz) indicate that InSe/GaSe/Si(111) has the potential to provide a practical, scanned-probe storage medium with areal densities exceeding a terabit/in^2.

4:00 PM HH2.7
Room Temperature Dielectric Function of Low-Dimensional $TlMeX_2$. Nazim Mamedov, Kazuki Wakita, Seiji Akita and Yoshikazu Nakayama; Physics and Electronics, Osaka Prefecture University, Sakai, Osaka, Japan.

$TlMeX_2$ (Me=Ga,In; X=S,Se,Te) incommensurate materials with one dimensional (1D) and 2D lattice structure continue to attract strong attention for their large thermoelectric power[1)], interesting non-linear electric and optical properties[2,3)], photo-induced memory effects[4,5)]. Expected feasibility of nanorod and nanoplate preparation, which can provide a wide area for new applications and basic science developments, is now under examination using advanced nanomanipulation technique developed recently[6,7)]. In particular, we are going to experimentally investigate dielectric function spectra of the above nanoobjects, using some innovative optical approaches. In this work we present experimental data and analyses for room temperature dielectric function obtained ellipsometrically on bulk samples of all $TlMeX_2$ in the photon energy range 0.8-6.5eV by using a Jobin-Yvon spectroscopic phase modulated ellipsometer. Tensor components of dielectric function of anisotropic $TlMeX_2$ have been retrieved from multi-angle-of-incidence ellipsometric data taken for non-depolarizing samples in principal orientations of the plane of incidence regarding the axes of dielectric tensor. Energy gaps of the materials are obtained and further verified on depolarizing samples within incoherent reflection model. Discussions are given with references on electronic structure and possible consequences at the nanoscale. References 1) K. Okazaki et.al, Phys. Rev. B **64**, 045210 (2001); 2) M. Hanias et al, Phys. Rev. B **43**, 4135 (1991); 3) N. Mamedov et al, Jpn. J. Appl. Phys. **32**, Suppl. 32-3, 763 (1993); 4) H. Uchiki et al, J. Luminescence **87 – 89**, 664 (2000); 5) A. Kato et al, J. Phys. Chem. Solids (2003) in press; 6) H. Nishijima et al., Appl. Phys. Lett. **74**, 4061 (1999); 7) S. Akita et al., Appl. Phys. Lett. **79**, 1691 (2001).

4:15 PM HH2.8
Transition temperature variations of VO2 films caused by as-deposited residual stresses. Kuang Yue Tsai[1], Tsung-Shune Chin[1,4], Han Ping David Shieh[2] and Cheng Hsin Ma[3]; [1]Materials Science and Engeering, National Tsin Hua University, Hsin Chu, Taiwan; [2]Institute of Electro-Optical Engineering, National Chiao Tung University, Hsin Chu, Taiwan; [3]Materials Science and Engineering, and Frederick Seitz Materails Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois; [4]National Lien-Ho University, Miao-Li, Taiwan.

VO2 is a material with reversible thermo-chromic properties with a typical phase transition temperature (Tr) of 67oC, accompanying changes in crystal structure,optical and electrical properties. With different processing conditions during thin film depositions by rf-magnetron sputtering on glass substrates,different transmittance loops will be resulted upon thermal cycling. The films were further characterized using X-ray diffractometry (XRD) and ESCA. It was found that the residual stress of the thin films, as determined from XRD, is an important factor responsible for the variation in Tr. The another study, ESCA spectra showed that the difference in the binding energy of the two electrons:2P 1/2 and 2P 3/2 of vanadium atom is also proportional to the increase of residual strss. The bond length between vanadium and oxygen at room temperature, varied by the residual stress, affects the movement of both atoms during phase change and hence the Tr of VO2 thin films. The relationship between residual stress of as-deposited VO2 films and the relative position of vanadium and oxygen will be also delineated in details.

4:30 PM HH2.9
Memory effects in manganese perovskites. Natalia Noginova, Geoffrey Chellule, George B Loutts and Mikhail A. Noginov; NSU, Norfolk, Virginia.

Manganese doped perovskites are promising materials for non-magnetic data storage. Systems with low doping concentration, such as Mn:$YAlO_3$ are high quality optical crystals, demonstrating significant photorefractive effect [1]. Optically and electrically induced quasi-permanent change in low-field conductivity was observed in the materials with high concentration of manganese such as single crystals and films of $LaGa_{1-x}Mn_x0_3$ (x= $0.1 \div 1$). These memory effects can last for a long time at room temperature and can be easily erased by heating up to 230K. We explain our experimental results by photo induced or thermo induced local phase transition with the oxidation of Mn. 1. G. B. Loutts *et al.* "Manganese-doped yttrium orthoaluminate: A potential material for holographic recording and data storage", Phys. Rev. B, 57, pp. 3706-3709 (1998)

4:45 PM HH2.10
Binary and ternary chalcogenide films and changes of their properties with exposure. Miloslav Frumar[1,3], Tomas Wagner[1,3], Petr Nemec[1,3], Jaroslav Jedelsky[3], Jan Guttwirth[1,3] and Bozena Frumarova[2]; [1]General and Inorg. Chem., University of Pardubice, Pardubice, Czech Republic; [2]Joint Laboratory of Solid State Chemistry, University of Pardubice and Inst. of Macromolecular Chem. of Czech Acad. Sci., Pardubice, Czech Republic; [3]Research Center LN00A028, University of Pardubice, Pardubice, Czech Republic.

M.Frumar, T.Wagner, P. Nemec, J. Jedelsky, J. Gutwirth and B. Frumarova, University of Pardubice, Czech Rep. Films of binary and ternary chalcogenides of the systems A14-B15-C16, B15-C16 and

Ag-B15-C16 were prepared by thermal evaporation, spin coating and pulsed laser deposition (A14, B15, C16 is for elements of 14th, 15th and 16th groups of periodic table). The prepared films were exposed by continuous and pulsed laser light of different wavelengths and intensities (repetition frequences). The changes of the structure, optical and other physicochemial properties were studied and discussed. Both phase changes and photostructural effects were found.

SESSION HH3: Phase Change Mechanisms and Modeling
Chairs: Motoyasu Terao and David C. Wright
Wednesday Morning, December 3, 2003
Hampton (Sheraton)

8:30 AM *HH3.1
Optical And Thermal Aspects Of The Phase-Change Media Of Optical Data Storage. Masud Mansuripur, University of Arizona, Tucson, Arizona.

The phase-change (PC) media of optical data storage are typically deposited in thin film form on a plastic substrate, sandwiched between protective dielectric layers that play a significant role in determining the storage medium's optical and thermal behavior. In addition, rewritable PC media employ a thin metal film (e.g., Al-Cr alloy) to optimize the absorption of the focused laser beam during writing/erasure, to enhance the contrast between amorphous marks and the crystalline background during readout, and to promote rapid thermal quenching that is so critical to amorphous mark formation during recording. Several techniques are available for measuring the optical and thermal properties of the PC media. The most relevant techniques, however, are those that extract the optical and thermal constants of the PC layer (as well as those of the dielectric and metal layers of the stack) by performing direct measurements on the storage medium itself. The reason is that the real and imaginary parts of the refractive index, $n + ik$, the thermal conductivity K and, to a lesser extent, the specific heat C are dependent on the corresponding film thickness, on the nature of the substrate, on the deposition conditions, and on post-deposition treatment of the storage medium. Any measurements on bulk samples or on samples prepared under different conditions than those employed during media manufacture are likely to lead to inaccurate estimates of the parameter values. This tutorial describes an ellipsometric system specifically designed to measure the optical constants of PC optical recording media. Reflection and transmission measurements are performed on monolayer, bilayer, trilayer, and quadrilayer samples at angles of incidence ranging from 10° to 80°, while the sample is immersed in index-matching fluid to eliminate its substrate's effect on sensitive measurements. The extracted optical constants include the thickness and the n, k values of various layers, including those of the PC layer in amorphous and crystalline states. Also described is a two-laser static tester designed to write amorphous marks on crystalline media as well as crystalline marks on amorphous media. This system monitors a sample's reflectivity before, during, and after the application of a laser pulse, thus allowing the extraction of melting temperature T_m, specific heat C, and thermal conductivity K of the various layers within the stack. The combined set of optical and thermal parameters of the PC stack thus obtained enables one to simulate the recording/erasure processes, and to optimize the design of media for high-density optical recording.

9:00 AM *HH3.2
Investigation of Optical Property and Phase Transformation Kinetics of Ge-Sb-Te-(N) Alloy Thin Films by using Ellipsometry. Sang Youl Kim, Molecular Science & Technology, Ajou University, Suwon, Kyunggido, South Korea.

The optical property and the crystallization kinetics of Ge-Sb-Te-(N) alloy thin films are intensively studied by using ellipsometry. A numerical inversion technique of spectro-ellipsometry data is applied to get the complex refractive index spectra of either amorphous phase or crystalline phase, of thick films. The surface micro-roughness is estimated from AFM images and its effect is considered in ellipsometric data inversion. Multiple angle of incidence spectro-ellipsometry is found to be better suited to characterize thin films. The simulated reflectance spectra using the calculated complex refractive index show excellent agreement with the measured ones, where the difference is less than 1 % in the entire spectral range of 400-800 nm. Even though the composition of Sb in the stoichiometric Ge2Sb2Te5 is varied in its relative fraction from 22 % to 26 %, its optical property shows no change at all. On the contrary, the complex refractive index shows a monotonic variation on nitrogen addition. As the nitrogen concentration in Ge-Sb-Te-(N) increases from 0 % to 13.8 %, both the refractive index and the extinction coefficient of amorphous phase decrease monotonically. The extinction coefficient of crystalline phase shows a similar monotonic decrease except for much drastic behavior. The refractive index of crystalline phase shows a mixed behavior such that the decreasing behavior is observed above 680 nm and the increasing one below 680 nm. From the analysis of the ellipsometric phase transformation isotherms obtained at intermediate temperatures, crystallization constants such as Johnson-Mehl-Avrami exponent and the activation energy of each step of the cascaded phase transformation are determined. The conventional model of nucleation and crystal growth, followed by an anomalous grain growth of the second stage, is independently confirmed by SEM images and ex situ spectroscopic ellipsometric observation of wavelength dependent depolarization effect of samples quenched at each pre-selected stage of crystallization process. Ultrafast ellipsometer consisted of the division-of-amplitude- photopolarimeter as the polarization state detector is fabricated to investigate the phase transformation kinetics of Ge-Sb-Te at elevated temperatures. With its nanosecond resolution, this time resolved ellipsometer (TRE) can be ideal to get the ultrahigh speed ellipsometric response of Ge-Sb-Te. TRE data of Ge-Sb-Te irradiated by a laser pulse of 7 ns width has been collected for the first time. It is believed that understanding of phase transformation of Ge-Sb-Te at elevated temperature could contribute by a significant amount to the development of a reliable phase change optical storage device with a stable characteristics under repeated erase/write cycles.

9:30 AM *HH3.3
Simulation of Crystallization processes in phase change optical discs. Berangere Hyot[1], Ludovic Poupinet[1] and Pierre Jean Desre[2]; [1]CEA/LETI, Grenoble, France; [2]LTPCM, CNRS/INPG, Grenoble, France.

A fast algorithm has been developed to simulate the amorphization and crystallization processes of phase change material in optical storage. The software includes both optical and thermal models which give access to the spatial and temporal temperature distribution inside the multilayer structure even with a moving laser beam and a specific writing strategy. A physico-chemical model of crystallization is also incorporated to simulate the nucleation and the growth of nuclei. It takes into account the chemical nature of the adjacent layers, the transient temperature effect (50K/ns) and the stabilization of the amorphous state when the phase change material layer becomes thinner. The model is capable of simulating kinetics and microstructure during crystallization. This model development also includes exhaustive characterizations of the materials: spectroellipsometry, thermal conductivity estimation, static amorphization and crystallization of phase change material. The crystallization studies of thin films under laser irradiation are very helpful because they allow to guide the development of future-generations optical discs but they become also, more and more, a powerful tool to optimize new structures in microelectronics. For example, the simulation is a mean to determine the best annealing conditions to obtain the crystalline phase of "high K" materials or amorphous silicon involved in low thermal budget integrated device fabrication processes.

10:30 AM *HH3.4
Phase Change Materials By Design? Matthias Wuttig, I. Institute of Physics, RWTH Aachen, Aachen, Germany.

At present, phase change media that can met the increasing demands of modern storage technology are developed in industrial and university labs by employing experimental optimization schemes. Here we present an alternate approach, which is based upon the combination of combinatorial techniques to produce sample libraries and ab initio calculations of the ground state structure and the electronic respectively optical properties of binary and ternary Tellurium alloys. For a large number of samples it could be shown that only those samples with a particular group of structures enabled phase change recording. All materials that showed the required optical contrast between the amorphous and crystalline state had cubic or near-cubic structures, while materials based upon tetrahedral structures showed insufficient contrast. The different behavior of these two groups of materials could be explained in part by density functional theory which has been employed to determine the density of states, the band structure and the total energy for different structures of GeTe and GeSbTe based alloys as well as ternary alloys containing Ag, In, Sb and Te. The calculations show a variation of ground state structures and bonding type with stoichiometry. Understanding the observed trends promises the directed optimization of future phase change media. Contributions by Ralf Detemple, Daniel Wamwangi, Stefan Ziegler, Zheru Zhang, Henning Dieker, Meng-Bo Luo, Martina Mueller and Woijiech Welnic are gratefully acknowledged.

11:00 AM HH3.5
TEM study of InSbTe crystal morphology as a function of crystallization conditions. Marcel A Verheijen[1], Andrei Mijiritskii[2] and Bart J Kooi[3]; [1]Philips Centre for Industrial Technology, Eindhoven, Netherlands; [2]Philips Research Laboratories, Eindhoven, Netherlands; [3]University of Groningen, Groningen, Netherlands.

Apart from an amorphous phase, most phase-change materials suitable for rewritable optical media possess two crystalline states. These different crystalline states exhibit different optical properties and crystallization behavior and, therefore, influence recording performance. The difference in the two latter states is generally assigned to different crystallographic phases: cubic and rhombohedral. In this work crystallization of an InSbTe alloy is studied. Two different crystalline states can be formed in a thin InSbTe layer depending on crystallization conditions. These two states give rise to different reflectivity levels of the recording stack as well as a different level of normalized media noise. In contradiction to what was thought before, transmission electron microscopy analysis reveals that the two states have the same rhombohedral Sb-type crystal structure. What is different, however, is the morphology of the layer. In the present study the effect of several disc initialization parameters (laser power, number of initialization cycles, disc speed) on the crystallographic phase, texture, crystal width & length, lateral homogeneity has been studied. The phase-change layer is strongly textured, showing both an in-plane fiber texture as well as a texture component perpendicular to the plane of the layer. For both morphology types the out-of-plane texture can be described by a mixture of two principal texture components: [0-111] and [02-21]. The main morphological difference between the two types is a 45 degree rotation of the in-plane component of the texture. Crystallites in both morphology types have elongated shapes with an aspect ratio of 1:50-100. The long axis of these crystals is running parallel to the direction of procession of the laser spot. Additionally, the two types display differences in crystallite size and internal grain boundary structure. The two types of texture correlate to two distinct temperature budget regimes, this budget being a function of all initialisation parameters mentioned above.

11:15 AM HH3.6
In-Situ Tem Study of the Crystallization of Ge-Sb-Te Thin Films For Phase-Change Optical Recording. Bart Jan Kooi, Willemijn Groot and Jeff De Hosson; Applied Physics, University of Groningen, Groningen, Netherlands.

Using Transmission Electron Microscopy with in-situ heating, crystallization of amorphous thin films (in-between 10 and 70 nm thick) of Sb3.6Te with 0, 4 and 16 at.%Ge and of Ge2Sb2Te5 was studied. Adding Ge to Sb3.6Te strongly increases the crystallization temperature (Tc); 95, 155 and 220 0C for 0, 4 and 16 at.% Ge, respectively. Adding Ge also increases the nucleation rate, leading to smaller crystallites. Sb3.6Te crystals with 0 and 4 at.% Ge followed a linear growth mode (interface-controlled crystallization) and from an Arrhenius plot (logarithm of the growth-front velocity versus the reciprocal temperature) an activation energy for growth of 1.58+-0.1 and 2.37+-0.1 eV was derived for 0 and 4 at.% Ge, respectively. The crystallite size after iso-thermal transformation does not change significantly as a function of temperature implying that the activation energy for nucleation is similar to the one for growth. On the other hand the crystallite size is a function of film thickness, i.e. the smaller the thickness the smaller the crystallite size. Strong preference for nucleation with the [0001] axis perpendicular to the surface was observed, but during lateral growth this axis continuously tilts towards the in-plane direction. Important to note that during this special 'transrotational' growth mode the crystal surface remains flat. Typical tilts are observed of 10 degree per 300 nm. This crystal-growth mode is common for the so-called fast-growth phase-change films, but up to now not recognized. It will be shown that in-situ TEM is a powerful tool to study the crystallization (kinetics) of amorphous thin films. Nevertheless, the drawback is that the nucleation rate is easily affected by the electron beam of the TEM. We demonstrated this by a systematic study of the effect of the accelerating voltage and the current density of the electron beam on the incubation time for crystallization of Ge2Sb2Te5.

11:30 AM HH3.7
Modeling InSe Phase-change Materials. Krisztian Kohary, Victor Burlakov, Duc Nguyen-Manh and David Pettifor; Materials, Oxford University, Oxford, Oxfordshire, United Kingdom.

Indium monoselenide is a phase-change material: both the crystalline and the amorphous phases are stable at room temperature[1]. Beside applications such as solar cells and ionic batteries, InSe has recently attracted considerable attention because of its potential application as an optical recording medium. Amorphous spots (~100 nm) have been created and annihilated by short laser pulses in the epitaxial films[2,3]. The structural, electrical and optical properties need to be well understood before the device can be optimized. Crystalline InSe is a layered hexagonal semiconductor with anisotropic transport properties. However, much less is known about the structure and other physical properties of the amorphous phase. We performed first principles tight-binding molecular dynamics simulations to study amorphous InSe systems. Our studies involve other amorphous indium-selenide systems as well (In2Se3 and In4Se3). The three-dimensional amorphous networks with different densities were prepared by quick quenching from the liquid phase. The characteristics of the short-range order like radial distribution functions, coordination numbers, bond angle distributions, and ring statistics have been analyzed. We also addressed the structural stability of amorphous spots in the crystalline matrix. We performed atomistic Monte Carlo simulations to model the interface of amorphous and crystalline regions. These calculations were then compared with analytic calculations. [1] T. Nishida, M. Terao, Y. Miyauchi, S. Horigome, T. Kaku, and N. Ohta, Appl. Phys. Lett. vol50, 667 (1987) [2] A. Chaiken, G.A. Gibson, K. Nauka, C.C. Yang, B.-S. Yeh, R. Bicknell-Tassius, J. Chen, J. Jasinski, Z. Liliental-Weber, and D.D. Lindig, "Reversible optical recording on epitaxial indium selenide phase-change media" (abstract submitted to 2003 MRS Fall Meeting (Boston)). [3] G.A. Gibson, A. Chaiken, K. Nauka, C.C. Yang, R. Davidson, A. Holden, D.D. Lindig, R. Bicknell-Tassius, J. Chen, H. Liao, D. Neiman, D. Shut, S. Subramanian, B.-S. Yeh, J. Jasinski, Z. Liliental-Weber, "An Electron-Beam Addressed Phase-Change Recording Medium", (abstract submitted to 2003 MRS Fall Meeting (Boston)).

11:45 AM HH3.8
Crystallization Kinetics of Thin Films of Amorphous Te Alloys used for Optical Data Storage. Johannes Kalb[1,2], Frans Spaepen[1] and Matthias Wuttig[2]; [1]Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts; [2]I. Physikalisches Institut, RWTH Aachen, Aachen, Germany.

The crystal nucleation frequency and the crystal growth velocity of sputtered amorphous $Ag_{0.055}In_{0.065}Sb_{0.59}Te_{0.29}$, $Ge_4Sb_1Te_5$ and $Ge_2Sb_2Te_5$ thin films were determined as a function of temperature. Crystals were directly observed using ex-situ atomic force microscopy, and their change in size after each anneal was measured. In the temperature regime around and slightly above the glass transition temperature, these materials exhibited qualitatively similar crystal growth characteristics, but differed in their crystal nucleation characteristics. These observations are in line with earlier observations of the re-crystallization of amorphous laser-induced spots of these materials.

SESSION HH4: Phase Change Materials for Optical Disk Applications
Chairs: Andrei Mijiritskii and Han-Ping D. Shieh
Wednesday Afternoon, December 3, 2003
Hampton (Sheraton)

1:30 PM *HH4.1
Effect of Ionic Bond in Recording Materials on Characteristics of Phase-change Optical Disk. Motoyasu Terao, R and D Group, Hitachi. Ltd., Tokyo, Japan.

There is no easily understandable model to explain why addition of some metallic elements to a phase-change recording material speed up the crystallization. Crystallization mechanism is very complicated, however, simple model will be able to explain most of crystallization features. This paper proposes a crystallization model that takes difference of covalent bond and ionic bond into consideration. Ionic bond makes crystal-nucleation easier than covalent bond bacause ionic bond is more flexible than covalent bond. An example of changeable ionic bond between a metal and a chalcogenide element is a charged defect formation in Ag-chalcogenide compound. This can be an effective trigger of crystal nucleation. However, in ionic-bonding chalcogenides, motive force for chain-reaction type crystal growth is weaker than network forming covalent-bond chalcogenides in low temperature range. The decrease of crystal growth speed in low temperature range is partly caused by the fact that metallic plus-ion having small atomic number, for example Ti, has small diameter and decreases spaces between large minus-ions and stabilizes. In high temperature range, crystal growth speed becomes large because spacing between minus-ions increases by thermal motion to make atomic-arrangement change much easier and chain reaction is caused by thermal motion to make atomic-arrangement change much easier and chain-reaction is caused by thermal motion of ions. These phenomena make crystallization activation energy large. This is very good to obtain long storage life and high durability against read laser beam and high erasability. However, too much addition of ionic compound decreases storage life because many plus-ions become to move interstitial or charged defect positions. Elements having electronic negativity far from that of Te or Sb has a tendency to form ionic bonds. Addition of Tb or In is reported to make crystallization faster. Tb and In are considered to make chemical bonds having more ionic characteristics than Ge. In the case of already reported Sn or Bi addition, large ion diameter contrary to above mentioned Ti seems to increase crystallization speed. Introduction of ionic bond is also desirable in obtaining suitable recording-film characteristics for multi-layer optical disk in terms of high optical transmittance.

Because ionic bond that is bonding with long distance elements in the periodic table, makes optical band gap larger and increases transmittance of visible light.

2:00 PM *HH4.2
Media Technologies for 20GB Single Layer and 36GB Dual Layer Phase Change Rewritable Disc "AOD". Sumio Ashida[1], Keiichiro Yusu[1], Tsukasa Nakai[1], Takayuki Tsukamoto[1], Katsutaro Ichihara[1], Noritake Ohmachi[2], Naoki Morishita[2], Akihito Ogawa[2] and Naomasa Nakamura[2]; [1]Storage Materials and Devices Lab., Corporate Reserach and Development Center, Toshiba Corp., Yokohama, Kanagawa, Japan; [2]Optical Disc Development Dept., Core Technology Center, Digital Media Network Company, Toshiba Corporation, Yokohama, Kanagawa, Japan.

It is desired that a phase change media for the system with blue-violet laser diode has the capacity of 20GB or more considering an important application is recording high-definition moving pictures. Assuming the same ratio of the beam spot size to the mark size of the current DVDs, the estimated capacity for a blue-violet system is only 12 GB for the same NA. Although it is possible to achieve larger capacities by using higher NA along with thinner cover sheet of around 0.1 mm thickness, we have chosen 0.6-mm thick substrate with the NA of 0.65 ("AOD") because of a number of benefits. For example, designing a pickup that has the compatibility with CDs and DVDs is easy. Also, the manufacturing of the media is possible by the facility for current DVDs with only slight modification even for the dual-layer discs. We have achieved the capacity of 20GB for a single layer and 36GB for a dual layer rewritable AOD media by incorporating the most up-to-date signal processing and media technologies. Challenges in developing the media were to assure sufficient signal amplitude for shorter bit pitches and to lower the cross erase for narrower track pitches. To increase the signal amplitude, we applied a new recording material and optimized its composition. To lower the cross-erase, we used a "thermal control layer" that enabled the narrower track pitches by reducing the cross-erase. What is important for the dual layer media are the choice of the most appropriate interface film material for the semitransparent layer which is closer to the light incidence. The heat sink film and fine adjustment of the reflectivity that compensate the smaller signal amplitude are also important. In the presentation, we will discuss the details of each items listed above and the current status of our development.

2:30 PM *HH4.3
Phase change media for high density recording with PRML detection. Shuichi Ohkubo, Eiji Kariyada and Tatsunori Ide; NEC corporation, Kawasaki, Japan.

We have developed phase change media for high density recording using 0.6-mm-thick polycarbonate substrate. For reducing cross erase, in addition to the low-to-high recording polarity, nucleation dominant GeTe-Sb2Te3 pseudo-binary recording film rather than gorwth dominant one was used. Also, we have found that the addition of certain content of Indium to pseudo-binary film is effective in raising crystallization temperature resulting in the reduction of cross erase. It has been confirmed that the addition of Indium improves crystallization speed. as well as cross erase characteristics. The addition of Indium also enhances the difference of optical constants between the amorphous and the crystalline states, and thus, leads to improvement of signal quality. The R/W characteristics measurements were carried out using the developed phase change media consisting of Al-Ti/ZnS-SiO2/GeCrN/GeInSbTe/GeCrN/ZnS-SiO2/SiO2/ZnS-SiO2/PC sub. Wavelength and NA of the optical head were 405 nm and 0.65. The groove pitch of the substrate was 0.68 μm, and thus, the track pitch in the land/groove recording was 0.34 μm. The linear bit density was 130 nm/bit, using (1-7) RLL code. These values of the track pitch and the bit density leads to the recording capacity of 20 GB/side. The bit-error-rate (BER) was measured using PRML detection. The target PR was (1,2,2,2,1) which suppress noise enhancement in equalization under such high density recording conditions. The BER around 1e-5 has been obtained after 10 direct-overwrites with influence of both cross talk and cross erase. Thus, the recording capacity of 20 GB can be achieved with low-to-high phase change media and PRML detection. Also, we confirmed that the recording density near the optical cut-off was feasible by optimizing the write strategy.

3:15 PM *HH4.4
Blue Laser Inorganic Write Once Media. Bing Mau Chen, Hung-Fa Chen, Ru-Lin Yeh Yeh and Jei-ming Chung; R&D Division, Media Business group, Ritek Corporation, Hsin Chu, Taiwan.

With the advantages of low cost, portability and compliance with ROM disk, write once media have become the most popular storage media for computer and audio/video application. Several write once recording materials, such as TeOPd and Si/Cu have been proposed to realize inorganic write once media. Moreover, we propose AlSi alloy to be used for recording layer of write once media. The intrinsic properties of disk were studied by static tester that is a writing-reading optical system providing images of the change of structure and measurement of the reflectance. As AlSi thickness of 50 A, the recorded marks were created when the laser pulse duration is larger than 20 ns with writing power of 12 mW. The reflectivities of recorded marks are larger than that of un-recorded marks. Similar properties were observed in the AlSi thickness of 75 A. On the contrary, the reflectivity of recorded mark is smaller than and that of un-recorded marks when the thickness of AlSi alloy is 125 A. The similar characteristics were observed in the AlSi thickness of 200 A. The RLL(1,7) random data were recorded by the optical disk tester from Shibasoku Inc (405 nm, NA=0.65) under 66 MHz clock frequency and 8.25 m/s linear speed. As AlSi thickness of 50A, according to the sum signals of disk before and after writing, it exhibits that the disk is a low to high write once medium. The jitter value is less than 8 % and the modulation value is larger than 0.5. On the contrary, the signal polarity of sum signal of disk with AlSi thickness of 200A was reverse; it reveals that disk is a high to low write once medium. The jitter value is less than 8 % and the modulation value is larger than 0.5 at writing power of 6 $\sim$ 7 mW.

3:45 PM *HH4.5
Marerials Science for Ultra Density Optical. Robert Somekh, Plasmon Data Systems Ltd., Royston, United Kingdom.

Ultra Density Optical (UDO) has been designed as the Phase Change successor to five and quarter inch Magneto Optic data storage products, with a UDO road map spanning three product generations leading to 120GB capacity. First generation UDO will utilise 405nm wavelength, 0.7NA drive optics with 100 micron cover layer media construction in a robust, double-sided cartridged format with 30GB capacity. There will be two types of UDO, both aimed at the professional market: UDO Write Once for high density, high data rate, archival data storage applications, and high cyclability UDO Rewritable. The features of UDO and the underlying Media Engineering optimisation strategies are discussed The write once media for UDO is based on a formulation first introduced by Kodak(1) and is based on a mixture of a chalcogenide material (Sb-In-Sn) and a dielectric (ZnS-SiO2). The advantage of this material is that it combines high speed performance with a tunable, low imaginary refractive index, k, which makes it very suitable for dual layer applications. UDO rewritable is based on a more conventional, so called, Fast Growth Material using extra layers to enhance its cyclability. This paper will discuss some materials issues associated with these media. In particular the wide range of time scales will be discussed in terms of atomic movements during the writing process, compared to the reading process and the storage processes. (1) Y-S Tyan, T.R.Cushman, G. Farrugia, G.R.Olin, B. Primerano, F. Vazan, Phase change recording element for write once applications U.S. Patent: US6,544,617,B1.

4:15 PM HH4.6
Mechanisms of Initialization of Doped Sb-Te Phase-Change Media. Samantha J Towlson[1], Clifford Alastair Elwell[1], Clare E Davies[2] and A Lindsay Greer[1]; [1]Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom; [2]Plasmon Data Systems Ltd., Melbourn, Royston, United Kingdom.

The doped Sb-Te family of chalcogenide thin films are of interest as the active layer in rewritable CDs and DVDs. As-deposited films of the low-reflectivity amorphous phase are initialized to form a crystalline layer in which data can be written by local melting and amorphization. The study is of initialization by scanned laser beam, and examines how the processing parameters influence the microstructure of the crystalline chalcogenide and thereby the performance of the disc. Controlling the initialization is critical to disc performance, particularly during the first few overwrite cycles. The microstructure of the chalcogenide active layer within discs is studied by plan-view transmission electron microscopy. The effects of laser power and disc velocity and composition are investigated. The crystal size, shape, phase identity and defect density are characterized, as well as reflectivity. The mechanism of initialization depends on the power absorption per unit area. Discs initialized at low powers or high velocities show microstructural features suggesting that crystallization is from the glassy state; at high powers or low velocities the crystallization is from the liquid state following transient melting. At low power the main crystal phase is face-centred cubic; at high power it is body-centred cubic. The consequences for disc performance, particularly in early overwrite cycles, are examined. To assist in understanding the mechanisms of initialization, comparison is made with microstructures generated by other scanned melting processes with a variety of materials.

4:30 PM HH4.7
Nano Structural Studies and Optical Properties of Multi-layer Chalcogenide Thin Film. Myung-jin Kang, Sae-young

Kim, Deok-hai Park and Se-Young Choi; Department of Ceramic engineering, Yonsei University, Seoul, South Korea.

Fast crystallization is a decisive factor for the achievement of high recording data transfer rates during phase change optical recording. In order to increase the data transfer rate of phase-change optical recording disks, a number of chalcogenide materials with fast crystallization speed were developed and a complicated disc structure with additional interface layers to enhance the crystallization speed of the recording media was employed. Recently, it has been reported that a multi-layer phase-change recording layer can be adopted within the phase change layer instead of the conventional single layer structure to accelerate the crystallization speed and enhance the structural stability of the phase-change layer. However, there has been no detailed report on the dependence of crystallization behaviors and optical constants of phase-change recording media on multi-layer structure. In this work, relationships between multi-layer structure and crystallization behaviors of phase-change optical media were discussed. A multi-layer phase-change recording layer of $GeTe/Sb_2Te_3$ was deposited by electron beam evaporation technique. The transmission electron microscopy (TEM) and grazing incidence x-ray diffraction (GIXRD) were used to characterize the crystallization behaviors. Optical constants were also investigated by using spectroscopic ellipsometer and UV-VIS spectrometer.

4:45 PM HH4.8
Changes in the Local Structure of Ge2Sb2Te5 Upon Reversible Crystallization-Amorphization. Alexander Kolobov[1], Anatoly Frenkel[2], Alexei Ankudinov[3], Paul Fons[4], Junji Tominaga[1] and Tomoya Uruga[5]; [1]CANFOR, AIST, Tsukuba, Ibaraki, Japan; [2]Physics, Yeshiva University, New York, New York; [3]Physics, University of Washington, Seattle, Washington; [4]Photonics Institute, AIST, Tsukuba, Ibaraki, Japan; [5]SPring8, JASRI, Kouto, Hyogo, Japan.

The crystalline phase has been studied previously and possesses an fcc structure [1], However, little is known about the structure of the amorphous phases. A technique suitable for investigation of the amorphous phase is EXAFS. It has been successfully applied to investigation of reversible photostructural changes in amorphous chalcogenides [2] and mixtures of amorphous and crystalline phases of the same atomic type [3]. Here we present the results of an EXAFS study of Ge2Sb2Te5. Measurements were performed on a real-device structure. To achieve better statistics and maximum confidence in the results, we have used concurrent multi-edge analysis. In the crystalline state we found that Te has Ge and Sb neighbours located at distances of 2.82 and 2.91 A. These distances are shorter than those expected from XRD [1]. The second-nearest Te-Te neighbour is located at a distance of 4.26 A which agrees very well with the lattice parameter determined from XRD. We suggest that Ge and Sb atoms are shifted to one of the Te neighbours. We further conclude that Ge and Sb vibrate predominantly in the direction perpendicular to the bond direction. For the re-amorphised state Te has both Ge and Sb neighbours located at distances of 2.60 and 2.84 A respectively, i.e. the bonds get longer. Our overall conclusion is that the local structure of the re-amorphised state is quite close to that of the crystallised state, this similarity being the reason for fast amorphous-crystalline transition. 1. T. Nonaka, G. Ohbayashi, Y. Toriumi, Y. Mori, and H. Hashimoto, Thin Solid Films, 370, 258 (2000) 2. A.V. Kolobov, H. Oyanagi, K. Tanaka, Phys. Rev. Lett. 87, 145502 (2001) 3. A. Frenkel, A.V. Kolobov, I.K. Robinson, J.O. Cross, Y. Maeda, C.E. Bouldin, Phys. Rev. Lett 89, 285503 (2002)

SESSION HH5: High Speed Resonse Phase Change
Optical Disk Technology
Chairs: Robert Somekh and Matthius Wuttig
Thursday Morning, December 4, 2003
Hampton (Sheraton)

8:30 AM *HH5.1
Explosive Crystallization in Eutectic Materials of Phase Change Optical Memory. Masahiro Okuda[1], Hirokazu Inaba[2] and Shoji Usuda[3]; [1]Okuda Tech. Office, Sakai, Osaka, Japan; [2]Osaka Prefecture Unv., Sakai, Japan; [3]Osaka Prefectural College of Tech., Neyagawa, Japan.

For the materials of eutectic composition using phase change optical memory, Sb rich recording layer have been utilized in order to rapid crystallization. But,the mechanism of excess Sb addition has not been clear, because an eutectic material is thought to cause the phase separation in its solidification process. Recently, it was reported that a melt-quenched crystalline states of eutectic AgInSbTe and SbTe with excess Sb has a quasi-equilibrium state with single phase hexagonal structure based Sb(R3m) and Sb atoms are randomly replaced with Te atoms. In this paper, we report the excess Sb effect for dynamics of rapid crystallization in eutectic amorphous films using the explosive effect. This crystallization mechanism describe the propagation with high velocity in the interface separating the crystalline and amorphous phase for Sb-rich eutectic materials. From these analysis, it is clear that the crystallization is grown up in the boundary of amorphous-crystalline region of eutectic materials, which is different from the stoichiometric Ge2Sb2Te5 madia. Under favorable conditions, an explosive crystalline process results by laser irradiation. Then, once crystallization has been initiated in amorphous-crystalline region, the entire amorphous films has been crystallized. Also, we studied the relation with the crystallization velocity v and the normalized latent heat q. From the non-linear heat conduction equation for 3 dimensional recording region, it is clear that the crystalline velocity v increases as q increases. From discussion on the effect of thermal history of Sb rich eutectic materials, it is concluded that the materials having more large latent heat q and the disk with ultra-rapid cooling structure are necessary to obtain the high line speed optical disk.

9:00 AM *HH5.2
Characterization of ultra-fast phase change optical disc with GaSb material. Kazunori Ito[1], Hiroko Tashiro[1], Makoto Harigaya[1], Katsuhiko Tani[2], Noriyuki Yiwata[2], Nobuaki Toyoshima[2], Akiko Kitano[3] and Kenichi Kato[3]; [1]Optical Memory R&D Center, RICOH COMPANY, Ltd., Yokohama, Japan; [2]Research & Development Center, RICOH COMPANY, Ltd., Yokohama, Japan; [3]Japan Synchrotron Radiation Research Institute, Hyogo, Japan.

Eutectic GaSb is expected as one of Sb-based rapid phase change materials for next ultra-fast rewritable optical disc at linear velocity higher than 28m/s. In this paper we present structure analysis of thin film eutectic GaSb with synchrotron radiation and characteristics of phase change optical disc with this material measured by static and dynamic tester. Crystal structure of thin film Ga12Sb88 is determined as the same structure as hexagonal Sb-structure. Rapid crystallization speed less than 30ns is obtained in static and dynamic erase test of amorphous recorded mark on DVD disc structure with this material. From the simulation of amorphous mark formation on this disc, the mechanism of this erasure process in this material is estimated as crystal growth from crystalline-amorphous boundary of recorded mark edge.

9:30 AM *HH5.3
Structural characterization of high-speed phase-change memory materials. Noboru Yamada[1] and Toshiyuki Matsunaga[2]; [1]Storage Media Systems Development Center, Matsushita Electric Industrial Co., Ltd., Moriguchi, Osaka, Japan; [2]Characterization Technology Group, Matsushita Techno Reseach, Inc., Moriguchi, Osaka, Japan.

Knowing the microscopic structures of phase-change materials greatly helps us to understand the various phenomena such as their remarkably rapid crystallization processes. We carried out powder diffraction studies on laser-annealed and powdered specimens using synchrotron radiation at SPring-8 and measured the electric resistance on film specimens. Either was done in the relation with temperature. The experiments were achieved on four materials: (A)GeTe-Sb2Te3, (B)AgInSbTe, (C) GeTe-(Sb,Bi)2Te3, and (D)GeTe-Bi2Te3. As a result, we have reached to obtain a mechanism model that will schematically explain rapid crystallization processes of these films as follows; i.e., i) these films crystallize into highly symmetrical crystal phase with cubic or quasi-cubic structure by laser annealing, ii) every crystal fundamentally has a cubic structure with a lattice parameter of 3A, iii) plural kinds of elements randomly occupied a same lattice site and iv) crystal states of these materials show just metallic characteristics; i.e., these materials show a tendency that they are not semiconductors but metals in the relationship between the melting point and the thermal linear expansion coefficient. It means that these materials show relatively larger atomic vibration in the solid state as compared with usual chalcogenide materials, and we think that the fact farther reduces the structure difference between amorphous and crystal states and works to accelerate their crystallization processes.

10:15 AM *HH5.4
Investigation of high speed phase transformation of phase change materials. T.C. Chong and L.P. Shi; Data Storage Institute, Singapore, Singapore.

This paper focuses on the study of thermally and optically induced phase transformation of phase change materials. Crystallization mechanism in phase change recording induced by scanning laser beam was studied by using a recently developed method. The disks were first written by a multi-pulse train and then erased using an erasing power which is lower than the smallest power required for one time complete erase. Laser-induced crystallization behavior was studied by observing oscilloscope signal change. Based on theoretical simulations and experimental results, an edge growth dominated nucleation

assistant model is proposed to describe the dynamic crystallization mechanism of the phase change optical disk. In order to increase the crystallization speed and data transfer rate, a superlattice-like structure (SLL) was applied to the recording layer of phase change optical discs. The SLL structure consisted of alternating thin layers of two different phase change materials, i.e., GeTe and Sb2Te3. The experimental results show that the SLL phase change optical disc exhibited excellent recording properties that could meet high-speed recording requirements. As the component ratio of GeTe/ Sb2Te3 increases, erasability increases at high speed indicating that crystallization speed increases. This result is contrary to the fact that the crystallization speed of the GeSbTe alloys decreases as the composition moves toward GeTe direction along the GeTe- Sb2Te3 tie line. It is mainly due to the structure adopted for the active layer, i.e., the SLL structure, which can prevent heat loss and reduce cooling rate in the active layer during laser irradiation at a high rotation speed. It was also shown that SLL phase change disks are suitable candidates for multispeed recording. The mechanism of this phenomenon is discussed by the proposed model. Ultrafast phase transitions triggered by single femtosecond laser pulse in GeSbTe films were investigated. By proper control of the film thickness, ultrafast crystalline and amorphous phase transformations have been achieved in GeSbTe films. These ultrafast phase transitions were confirmed by reflectivity change and X-ray diffraction measurement.

10:45 AM *HH5.5
Sb Based Materials For High-Speed Phase-Change Optical Recording. Dimitre Dimitrov, Ming-Hsun Hsieh, Shun-Te Cheng, Wei-Chih Hsu, Min-Jong Deng and Song-Yeu Tsai; ITRI, Hsinchu, Taiwan.

New phase-change rewritable optical recording materials based on GeSb and GaSb alloys for high-speed crystallization are studied. Optical properties, structure and crystallization temperatures of the recording films as well as multilayer stacks are measured. The influence of different dopants such as Sn, Ge, Sb, La, Ag and In on the physical properties of the recording films and phase-change recording characteristics is determined. It is found that crystallization temperatures decrease as the Sb content in GeSb and GaSb film increases. Ge or/and Sn doping is effectie for crystallization temperature improvement. GeSb and GaSb hyper-eutectic based thin film materials crystallized in single phase with only hexagonal Sb detected, the single-phase crystallization being one of the requirements for high-speed phase-change transitions. Amorphization and crystallization under violet laser (399nm) irradiation are studied by time-resolved reflectivity measurements. Both solid-state and melt-induced crystallization as well as partial recrystallization during amorphization are observed. The static tester experiments are used to separate the effects of annealing, melting, crystallization and amorphization on the temporal behavior of the reflectivity. GeSb and GaSb based disks with optimized structures shown high CNR and adequate erasability after recording layer composition and writing strategy optimization under blue laser dynamic testing. The phase-change alloys with compositions based on GeSb and GaSb eutectics are shown to be promising materials for high-speed blue laser recording.

11:15 AM HH5.6
Phase Cycling of GeSbTe- and AgInSbTe-Films Under Nanosecond and Picosecond Laser Pulse Irradiation.
Jan Siegel[1], Andreas Schropp[1,2], Javier Solis[1] and Carmen N Afonso[1]; [1]Instituto de Optica, CSIC, Madrid, Spain; [2]I. Physikalisches Institut A, RWTH Aachen, Aachen, Germany.

A permanent challenge in phase change optical recording is to push data transfer rates beyond current limits. We have set out to obtain ultrafast and reversible phase transformations in 50nm thick Ge2Sb2Te5, Ge4Sb1Te5 and Ag.055In.065Sb.590Te.290 (AIST) films on glass substrates using short ns and ps laser pulses. In our experiments, the samples are irradiated with single laser pulses of 30ps, 3ns and 6ns duration to induce phase transformations, while measuring in real-time the reflectivity evolution at the sample surface using a probe laser. This enables us not only to determine the transformation times (being usually the limiting factor for the data transfer rate) but also to obtain a much clearer physical picture of the transformation dynamics than that available from static measurements. For a fixed pulse duration (3ns) complete re-amorphization of crystalline areas could be induced in all samples by a single laser pulse, obtaining an optical contrast of as large as 20%. The fastest amorphization time (5ns) was observed for Ge2Sb2Te5. Partial re-crystallization (10% optical contrast) within less than 10ns could only be achieved for both GeSbTe compounds. Ge2Sb2Te5 was selected for a further study of the influence of the pulse duration. Re-amorphization times around 5ns were observed in all cases, apparently limited by the temporal resolution of the detection system. Partial re-crystallization was observed for pulses of 30ps and 3ns whereas a near-complete crystallization was induced by 6ns pulses, and the transformation process is completed within 15 ns. The different behaviour for 6ns is attributed to the lower cooling rate induced by the longer pulse, promoting the formation and growth of crystalline nuclei. We conclude that, for the samples studied, 6ns pulses combine in an ideal way the ability to induce complete and reversible transformations with the capability to induce transformation times of 15ns or less.

11:30 AM HH5.7
Dynamics of Ultrafast Phase Transitions in GeSbTe Films.
Qinfang Wang[1,2], Luping Shi[2], Kaijun Yi[2] and Tow Chong Chong[1,2]; [1]Electrical and Computer Engineering, National University of Singapore, Singapore, Singapore; [2]Data storage Institution, Singapore, Singapore.

Femtosecond pulse is promising for optical data storage due to its high data transfer rate and suppression of thermal diffusion. Our previous investigations revealed that ultrafast amorphization and crystallization induced by single femtosecond pulse could be achieved by proper control of Ge1Sb2Te4 film thickness, and intense femtosecond pulse also induced an ultrafast nonthermal phase change in amorphous Ge1Sb2Te4 films. The purpose of this study is to investigate GeSbTe system by measuring transient reflective intensity change with time-resolved microscope in order to gain insight into the dynamics of ultrafast phase transitions in GeSbTe system. Our in house developed Phase Change Optical Disk Design software was used to design the multilayer structures. Time-resolved microscopy was employed to measure the transient reflective intensity change as function of pump-probe delay time. A single shot of 130fs, P-polarized pulse at 800nm was produced by a regenerative amplifier, Ti:sapphire, which is pumped by a mode-lock femtosecond laser (Spectra physics). A 50% beam splitter divided this output into a pump beam, which was focused at normal incidence onto a sample surface (spot diameter approximately 200 mm), and a second beam, served as a probe beam and replaced the standard illumination of an optical microscope, was focused at near 45 degree incidence to a spot of approximately 2000mm diameter overlapping and illuminating the area excited by the pump pulse. A magnified image of the excited surface region was recorded at a given pump-probe time delay by collecting the specularly reflected light with a CCD camera. The sample was moved 500 mm after each laser shot by a compute-controlled stage in order that each laser shot interrogated a fresh region of the sample. The transient reflective intensity change reveals ultrafast dynamics in GeSbTe films triggered by intense femtosecond laser pulse.

11:45 AM HH5.8
Structure analysis of the amorphous thin films of GeSbTe compounds by grazing incidence X-ray scattering.
Masugu Sato[1], Toshiyuki Matsunaga[2], Takashi Kouzaki[2] and Noboru Yamada[3]; [1]Japan Synchrotron Radiation Reseach Institute, Mikazuki, Hyogo, Japan; [2]Characterization Technology Group, Matsushita Technoresearch, Inc., Moriguchi, Osaka, Japan; [3]Storage Media Systems Development Center, Matsushita Electric Ind. Co., Ltd., Moriguchi, Osaka, Japan.

The structures of the amorphous thin films of GeSbTe compounds, the materials for the recording layer of the phase-change optical memory, have been investigated by X-ray scattering measurement with synchrotron radiation in SPring-8. Thin films with compositions of $GeSb_2Te_4$ and $Ge_2Sb_2Te_5$ are deposited on Si substrates. Their X-ray scattering profiles are measured on grazing incidence condition and the electron radial distribution functions (ERDF) are derived. The ERDF profiles of samples with two compositions have been almost same. In the EDRF, peaks indicating atomic pair distribution are found around the radial distance of 2.8 Å, 4.2 Å and 6.2 Å. These peaks correspond nearly to the radial distances of the 1st (3 Å), 2nd (4.2 Å) and 5th (6.7 Å) neighbor atomic pairs with high electron density in the crystal structure, where their crystalline phase is the same NaCl-type. Furthermore, there are no significant peaks on ERDF around distance region corresponding to the 3rd (5.1 Å) and 4th (6 Å) neighbors with low electron density in the crystal. These results indicate that the structure in amorphous phase is very similar to that in crystalline phase over wide composition region.

SESSION HH6: High Density Optical Disk Technology
Chairs: Lanbertus Hesselink and Sang Youl Kim
Thursday Afternoon, December 4, 2003
Hampton (Sheraton)

1:30 PM *HH6.1
Multi Layer Disk Design For Near-Field Phase-Change Recording. koichiro kishima, Isao Ichimura, Kimihiro Saito, Kenji Yamamoto, Atsushi Iida and Kiyoshi Osato; Broadband Network Company, Sony Corporation, Tokyo, Japan.

Recently we have demonstrated experimental results of Near-Field Phase-Change Recording by developing an air-gap servo technique that realizes an optically contact condition between rotating medium and lens. The two-element lens consists of 1mm diameter super-hemispherical Solid Immersion Lens (SIL) with the index of 1.83 and objective lens of 0.45 Numerical-Aperture (NA) attains the NA of 1.5. 80nm/bit linear bit density has been demonstrated by a combination of a GaN blue laser diode. 50Gbit/in.2 areal density was also demonstrated by using tracking servo technique enabled by mounting the two-element lens on a two-axis actuator and developing the near-field phase-change medium. The medium has a shallow groove structure and a flattened surface performed by thin tri-layer cover. This cover layer restrains the decrease of readout signals from recorded marks when the air-gap is the designated value around 50nm. On the other hand in the research field of far-field optical data storage, the multi layer recording has been much interested despite its NA of 0.85. Our near-field optical head has almost same availability with commercially used far-field optical head except the 50nm working distance and the value of NA. In this talk we will report the approach of multi layer near-field recording that might double the recording capacity. The newly developed 1.5-NA near-field optical head using a GaN blue laser diode will be introduced. In this optical head the relay lens unit is used for the focus control on either recording layer and the liquid crystal panel is used for reducing the spherical aberrations. The newly designed multi-layer near-field phase-change recording medium will be also introduced. The high index material will be used in the intermediate region between recording layers to restrain the spread of laser lay. Considering the recording medium we also discuss about the design algorithm and fabrication methods.

2:00 PM *HH6.2
Optical Phase-Change Materials and its Great Role in 3rd Generation Super-RENS Disk. Junji Tominaga, Masashi Kuwahara, Takayuki Shima, Alexander Kolobov and Takashi Nakano; Center for Applied Near-Field Optics Research, AIST, Tsukuba, Japan.

The signal intensity of the newest super-RENS disk with PtOx recently marked CNR > 47 dB for 100-nm mark trains. However, the readout mechanism of the disk has not yet been revealed. Very recently, we noticed that heat accumulated in the recording film (AgInSbTe) plays a very important role in the strong signal from the small marks beyond the diffraction limit. In this paper, we examined the phase transition in detailed comparison with results estimated by differential scanning calorimetry (DSC) and by disk drive test analysis. Several other phase-change (PC) materials: Ge2Sb2Te5, GeTe, GeTe4, Sb2Te3, and AgSbTe2 were also examined. The sample structure for DSC consists of a multilayers: ZnS-SiO2 (15 nm)/PC (500 nm)/ZnS-SiO2(15 nm), which was directly deposited on an Al pan. The heat ramp rate was 30K/min and heat flow was monitored in N2 atmosphere. On the other hand, the structure for the dynamic disk drive analysis consists of ZnS-SiO2 (95 nm)/PC (30 nm)/ZnS-SiO2 (40 nm)/PtOx (3.5 nm)/ZnS-SiO2(95 nm), which was deposited on a pre-grooved polycarbonate disk. The recording and readout characteristics of the disk were carried out by 635-nm wavelength and 0.60 lens NA. Using a linear relationship between the laser power and temperature, and as-deposited amorphous-crystal transition temperature at a constant linear velocity (6 m/s) with dc and 8-MHz pulsed laser beam, we could find a very good correlation. Considering the reflection correction of each different PC disk, it was also found that all results converged on a specific line. According to the detailed analysis, it was revealed that the strong signal of the super-RENS within AgInSbTe occurs in a solid phase at 350oC-450oC, on the other hand, super-RENS within Ge2Sb2Te5 in a solid phase at 310oC-450oC. It is suggested that the super-RENS transition appears by the polarization catastrophy of the ferroelectric phases.

2:30 PM *HH6.3
Optical nonlinearity of silver oxide and its applications for volumetric optical disks. Fung Hsu Wu[1,2,3], Tom D. Milster[2,3,1] and Han-Ping D. Shieh[3,1,2]; [1]Institute of Electro-Optical Engineering, National Chiao-Tung University, Hsin-Chu, Taiwan; [2]Optical Science Center, University of Arizona, Tucson, Arizona; [3]Institute of Electro-Optical Engineering, National Chiao-Tung University, HsinChu, Taiwan.

A variety of optically nonlinear materials of organic films, polymers, metal or semiconductor dispersed glass, and super lattice multilayers have been discovered and developed. For storage applications, an optical switching technique was proposed by using its optical nonlinearity to multiply disk capacities on a disk substrate. In this paper, the optical nonlinearity of triple-layer silver oxide structure (ZnS-SiO2/AgxO/ZnS-SiO2) was investigated. Optical nonlinear properties were observed a function of the oxygen concentration. Nonlinearity of three different oxygen content samples, Ag3.2O, Ag1.7O and Ag1.4O, were studied. Only medium oxygen content sample, Ag1.7O, exhibits a strong nonlinearity that is not a function of the laser intensity. About 10% transmittance decreases as the sample approaches focus for all laser powers was observed. In a volumetric disk, light intensity activated optical switching layer can reduce laser energy decay and increase recording sensitivity while reading and recording, respectively. Therefore, triple-layer silver oxide structure, ZnS-SiO2/Ag1.7O/ZnS-SiO2, with light intensity dependent optical characteristics can be adopted as optical switching layer and modulate optical characteristics of recording layer in the disk to be highly absorptive or transmittance when laser beam impinged on it or not, respectively. Furthermore, a structure of multiple transparent films with such optical switching layer as recordable media is proposed to increase the number of recording layers in a volumetric optical disk. This optical switching layer for volumetric recording can optimize R/W performance, so that a sub-micron to nano order well-defined deformation area (mark) can be written precisely on the surface of transparent film by a focused laser beam. Thus, highly transparent film with optical switching layer as recording media can achieve more recording layers in one volumetric optical disk. Moreover, a change in the far-field pattern was experimentally observed when the sample Ag1.7O with positive nonlinear absorption coefficient b was placed at focus.

3:15 PM *HH6.4
Multi-Layer Phase-Change Media For High Capacity Far-Field Optical Data Storage. Michael Vincent Morelli[1], Mark McDonald[1], Tokuyuki Honda[2], Sergei Sochava[1] and Lambertus Hesselink[3]; [1]Optical Platform Division, Intel Corporation, Newark, California; [2]Canon Incorporated, Tokyo, Japan; [3]Stanford University, Stanford, California.

High capacity far-field optical data storage has been achieved without the use of blue light or high NA optics. This was accomplished by developing a novel multi-layer phase-change media and a drive based upon conventional DVD-R components. We present the design of this multi-layer media, which was demonstrated to achieve capacities greater than 10Gb per side and read/write/erase speeds in excess of 5Mb/s. Design trade-offs to realize 60K BPI 30K TPI, maximize layer SNR (minimize crosstalk), and optimize data and servo channel performance are described for a four data-layer design which was fabricated into a conventional 60um layer on a 5.25 inch disk. Details of the media's material selection, coupled optical-thermal design, and empirical characterization are explored along with enabling aspects of the drive's confocal read channel and dual wavelength servo.

3:45 PM HH6.5
Super-RENS Disk with a Deformative Mask Layer. Takayuki Shima[1], Masashi Kuwahara[1], Takashi Kikukawa[2], Toshio Fukaya[1], Takashi Nakano[1] and Junji Tominaga[1]; [1]Center for Applied Near-Field Optics Research, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; [2]Recording Media & Solutions Business Group, TDK Corporation, Saku, Japan.

Properties of super-RENS disk have greatly improved by selecting a deformative material as a mask layer. Kikukawa et al. has previously shown that silver oxide mask layer is not just for super-resolutional readout but also important as a recording layer making deformation-pits inside the disk structure [1]. We have recently selected platinum oxide (PtOx) [2] and metal-free phthalocyanine (H_2PC) as a mask layer that are also promising inducing the deformation when they are heated by the laser light. Disk samples were prepared by RF magnetron reactive sputtering and evaporation methods. A typical structure was polycarbonate disk substrate / ZnS-SiO_2 (thickness: 130 nm) / deformative mask layer (4-6 nm) / ZnS-SiO_2 (40 nm) / Ag-In-Sb-Te (60 nm) / ZnS-SiO_2 (100 nm). The disk properties were evaluated by an optical disk drive tester (DDU-1000, Pultec Industrial Co.) with the laser wavelength (λ) and the numerical aperture (NA) of 635 nm and 0.6, respectively. Recording and readout experiments were mostly performed for the 200 nm-size marks (constant linear velocity: 6 m/s, frequency: 15 MHz) that is smaller than the resolution limit (λ/4NA= 265 nm). In both material cases, super-resolutional readout was possible, and fairly high carrier-to-noise ratio exceeding 40 dB was obtained (46 dB for PtOx and 41 dB for H_2PC). Transmission electron microscope images clearly showed that the mask layer is deformed by the recording process. For PtOx, it is a result of the thermal decomposition to Pt (particles) and O_2 at the temperature around 850 K [3]. For H_2PC, it is brought by the sublimation and/or the decomposition. Recorded-mark shape was more rigid for PtOx mask case probably since it has a distinct recording-power threshold. It should be noted that there were obviously no metal particles precipitated for H_2PC mask case, and they are not necessary to be an origin of the super-resolutional readout. A possible readout mechanism will also be discussed. [1] T. Kikukawa et al., Jpn. J. Appl. Phys. 42, 1038(2003). [2] T. Kikukawa et al., Appl. Phys. Lett. 81, 4697(2002). [3] T. Shima and J. Tominaga, Jpn. J. Appl. Phys. 42, in print.

4:00 PM HH6.6
Nonlinear Characteristics of Super Resolution Chalcogenide Thin Film. sae-young Kim, Myung-jin Kang, Dong-han Lee and Se-young Choi; Department of Ceramic engineering, Yonsei univ., Seoul, South Korea.

A super-resolution near field structure is attractive technology for optical recording storage achieving high recording densities beyond the diffraction limit. In this point of view, it generates the near field interaction in a material itself in the structure and it satisfies the removability with both high-density recording and readout. Super-resolution technique can be realized by using self-focusing effect of materials that have high non-linear optical properties. Chalcogenide glass is one of the promising materials, which shows high non-linear properties and fast response time. Especially As-Se chalcogenide glasses have large non-linear optical properties. Therefore, feasibility of applying As-Se chalcogenide thin film to super resolution thin film was investigated. In this work, the relation between third-order optical non-linearity and composition of As-Se system is discussed. Chalcogenide glasses were fabricated and characterized by using differential scanning calorimetry (DSC) and X-ray diffraction (XRD). Chalcogenide thin films were deposited by thermal evaporation technique. Phase of the thin films were characterized by using grazing incidence X-ray diffraction (GIXRD) and transmittances of the thin films were measured by using ultraviolet-visible spectrometer. Optical absorption spectrum and refractive index of the thin film were measured by fitting the variable angle spectroscopic ellipsometer (VASE) data. In particular, nonlinear optical properties were characterized by using z-scan technique. Super resolution effects were measured by using Beam profiler from comparing the transmitted laser beam size of the thin films.

4:15 PM HH6.7
Nonlinear change of optical properties of Co_3O_4 films induced by nanosecond laser irradiation. Hiroki Yamamoto[1], Shuhei Tanaka[1], Takashi Naito[2] and Kazuyuki Hirao[3]; [1]Nanotechnology Glass Tsukuba Research Laboratory, New Glass Forum, Tsukuba, Ibaraki, Japan; [2]Hitachi Reseach Laboratory, Hitachi, Ltd., Hitachi, Ibaraki, Japan; [3]Division of Material Chemistry, Kyoto University, Kyoto, Kyoto, Japan.

Co_3O_4 thin films have great optical nonlinearity and their refractive index and extinction coefficient change reversibly by laser irradiation with wavelengths of 405 and 650 nm. Therefore they are applicable as super resolution films for next generation optical disks with high recording density. In order to confirm the mechanism, we studied the change of optical properties of the Co_3O_4 thin films induced by nanosecond pulse laser irradiation in various wavelengths. The Co_3O_4 films were obtained by rf magnetron sputtering on silica glass substrates at room temperature, and pure argon gas was used as sputtering gas. Change of optical transmittance of Co_3O_4 films was measured using nanosecond YAG-OPO laser system whose wavelength is tunable in the range from 410 to 2,400 nm. Pulse width of the laser was 5 ns. Optical absorption coefficient (α) of Co_3O_4 thin films increased as a function of laser intensity at λ=410 and 600nm, and a at λ=500nm showed no significant change, which was consistent with the change of a induced by thermal treatment. Increasing temperature by laser irradiation caused the absorption coefficient of the Co_3O_4 thin film. Pulse width of the laser was 5 ns, so the change occurs within 5 ns. Band gap shifts of Co_3O_4 by thermal treatment indicated that tetrahedral sites, including Co^{2+}, in Co_3O_4 normal spinel structure did not change so remarkably, but the bonding property of octahedral sites, involving Co^{3+}, had a significant change. Consequently, relative positions of cobalt ions changed, and then the dielectric properties and refractive index changed. Similar structural change of Co_3O_4 thin films occurred during laser irradiation.

4:30 PM HH6.8
Design of Holographic Recording Conditions with Optical Densities of Thick Azopolymer Films. Shin Yasuda, Katsunori Kawano, Jiro Minabe, Tatsuya Maruyama, Kazuhiro Hayashi and Yasuhiro Ogasawara; Corporate Research Group, Fuji Xerox Co., Ltd., Ashigarakami-gun, Kanagawa, Japan.

Azobenzene-containing polymers have drawn attention as rewritable holographic media. High storage density requires a thick recording film because the Bragg condition needs to be severe. However, as the film thickness increases, light absorption inside the film increases due to the increase of its optical density, leading to decreasing the ability of forming the grating inside the film. The more greatly the grating is attenuated in the film, the less severe the Bragg condition become. Thus, it is important to know the relation among optical density, grating attenuation and the Bragg condition in designing the performance of holographic memory system. We, therefore, evaluated the effect of optical densities in thick films on the Bragg condition using the shift-multiplexing method with a spherical reference wave. In addition, we introduced a theoretical equation for the shift-multiplexing optics that considered grating attenuation in a film. By blending azobenzene-containing polyester (azopolymer) and cyanobiphenyl-containing polyester, we fabricated four kinds of 250micron-thick films whose optical densities increased with azopolymer concentrations that ranged from 10wt% to 70wt%. As a result of the evaluation, a higher optical density produced a broader profile of shift selectivity, i.e., the Bragg condition became less severe. With our equation fitting the profiles of shift selectivity, we estimated the grating attenuation coefficients of the films. As a consequence, we confirmed that the film with a higher optical density had a larger grating attenuation coefficient: the coefficient of the film with 70wt% azopolymer concentration is approximately 10 times larger than that of the film with 10wt% azopolymer concentration. Moreover, we experimentally found the relation between the optical densities and the grating attenuation coefficients. Using this relation and our introduced equation, we can design the shift selectivity on a film with any optical density in the shift-multiplexing optics, so that holographic recording conditions can be designed.