

Nanostructured Materials in Information Storage

Zvonimir Z. Bandić, Dmitri Litvinov,
and M. Rooks, Guest Editors

Abstract

The ever-increasing demand for information storage has pushed research and development of nonvolatile memories, particularly magnetic disk drives and silicon-based memories, to areal densities where bit sizes are approaching nanometer dimensions. At this level, material and device phenomena make further scaling increasingly difficult. The difficulties are illustrated in the examples of magnetic media and flash memory, such as thermal instability of sub-100-nm bits in magnetic memory and charge retention in flash memory, and solutions are discussed in the form of patterned media and crosspoint memories. The materials-based difficulties are replaced by nanofabrication challenges, requiring the introduction of new techniques such as nanoimprinting lithography for cost-effective manufacturing and self-assembly for fabrication on the sub-25-nm scale. Articles in this issue describe block-copolymer lithographic fabrication of patterned media, materials studies on the scaling limits of phase-change-based crosspoint memories, nanoscale fabrication using imprint lithography, and biologically inspired protein-based memory.

We have been witnessing increasing demand for information storage since the very first IBM 350 disk drive with 4.4 megabytes of storage space was sold over 50 years ago. The growing amounts of both personal and Web-stored digital media content, accelerated by faster networks, and Web 2.0 represent just a few of the stimuli for an already rapidly growing storage demand. The data storage industry has traditionally answered this demand by providing increasing capacity in storage devices: magnetic-media-based hard-disk drives for personal and server-based storage and optical removable media and magnetic-media-based tapes for portability and archival uses. Additionally, solid-state drives based on silicon flash memory have recently emerged, offering compelling all-electronic nonvolatile storage devices without any moving parts. Such drives are widely available both as universal serial bus flash drives and as solid-state drives for mobile computers.

The key magnetic recording components of hard-disk drives are magnetic media (where information bits are stored) and

recording heads (which write to and read from the media). Magnetic media comprise a thin-film structure consisting of several nonmagnetic and magnetic thin films, capped with a thin (sub-5-nm) carbon film coating and a thin (sub-1-nm) lubricant layer. The information is stored in the CoCr-based thin film located close to the disk surface in the form of magnetic domains with perpendicular magnetic orientation, which are also called bits. The bits which are produced or written with a magnetic recording head that utilizes a write head to produce a varying magnetic field and write bits to the media. The bits are read back with the magnetic read head that utilizes the giant magnetoresistance effect to register changes in the magnetic orientation of the written bits.³ In the case of silicon flash memory, the information is stored as charge on the insulated floating gate of the metal oxide semiconductor transistor.

The increasing capacity of these devices has traditionally been achieved by improving the areal density to preserve constant volume, weight, and power demands of storage. The bit areal density is defined as

the number of bits stored per unit area of the (typically) two-dimensional storage devices. For example, in the case of magnetic-media hard-disk drives, areal density has increased over eight orders of magnitude in the past 50 years, and the device weight (measured per megabyte) has correspondingly decreased over eight orders of magnitude. These improvements have allowed for 320 gigabyte (GB) mobile disk drives weighing just slightly more than 100 g.

A perpendicularly oriented magnetic-media disk drive sold today typically has an areal density of 250 Gb/in.² (and this value is likely to be outdated by the time this issue of *MRS Bulletin* is published). Laboratory demonstrations have recently shown areal densities in the range between 420 Gb/in.² and 600 Gb/in.², which correspond to bit areas smaller than 1,500 nm². The area corresponding to one bit is typically 80 nm × 20 nm or smaller and is clearly well in the sub-100-nm range. Similarly, many manufacturers of silicon flash memories are upgrading their facilities for 45-nm production.

Further increases in storage capacity requirements will likely push bit sizes even smaller, to the point where further scaling of either magnetic thin-film or silicon-based storage devices becomes very difficult or impossible. A common example is the scaling of magnetic-media bits in magnetic hard-disk drives. This scaling is limited by the phenomenon where the energy required to switch the orientation of a particle's magnetic moment becomes comparable to the particle's thermal energy, or the superparamagnetic effect. The area corresponding to one bit of information is presently approximately 100 nm × 20 nm and contains approximately 50–100 grains with an average diameter of 8 nm. The size of the grains determines the effective signal-to-noise ratio, as the line roughness of the transition between two bits depends on the size of the grains. A reduction of the bit size (and an increase of the areal density) therefore requires a reduction of the average grain size. However, the grain volume cannot be arbitrarily reduced: the superparamagnetic limit is reached at the point when a grain becomes so small that thermal energy alone can flip its magnetization direction. The critical grain volume, V_{gr} , that determines the onset of the superparamagnetic limit is determined by the condition that the stored magnetic energy, $K_u V_{gr}$, remains about 40–60 times larger than the thermal energy, $k_B T$, where K_u and k_B are the magnetic anisotropy and the Boltzmann constant, respectively, and T is the temperature.¹ This implies that the

size of thermally stable grains should be larger than approximately 8 nm.²

Most of the scaling challenges are being addressed with media and disk head improvements,³ such as transitioning from longitudinal to perpendicular media. The current consensus in the hard-disk drive industry is that magnetic recording on continuous perpendicular media can be scaled to bit areal densities in the range of 500–1,000 gigabits/in.². In the long term, alternative technologies such as heat-assisted magnetic recording and patterned media are being considered as likely routes to terabit per square inch densities and beyond.

Silicon-based flash memories are facing scaling challenges as well, albeit quite different in physical nature. The core element of the flash memory is the floating-gate metal oxide semiconductor transistor that stores information as charge on the insulated encapsulated floating gate. The most significant challenge is the thickness of the oxide film required to isolate a floating gate. As the gate length is reduced (to increase the effective areal density), the oxide thickness has to be reduced proportionally. However, when the oxide thickness becomes approximately 8 nm or less, charge retention (or actual memory) becomes degraded through trap-assisted tunneling through the oxide.⁴ Even if the density of the positively charged clusters (traps) generated in the oxide during erase cycles can be controlled, reduction of the oxide thickness is limited to 6–7 nm because of an exponentially increasing tunneling current, unless new oxide materials are introduced.

Another scaling limitation is related to so-called read/write “disturb” capacitive coupling through parasitic capacitors around the floating gate that causes shifts of the threshold voltages of a cell proportional to the threshold changes in adjacent cells. As the device size is reduced, this capacitive coupling is more pronounced because of the smaller insulation thickness. In the short term, some of these challenges can be addressed by device design improvements, architectural improvements (such as storing multiple levels per cell), and attempts at three-dimensional integration. In the long term, transition to crosspoint memories based on non-silicon materials such as phase-change, ferroelectric, or magnetic materials will become required. Crosspoint memory, or crossbar memory, indicates a type of solid-state memory based on a matrix of active memory elements located at the intersection of two arrays of conducting lines.

Figure 1 shows the impact of nanostructured materials on information storage and

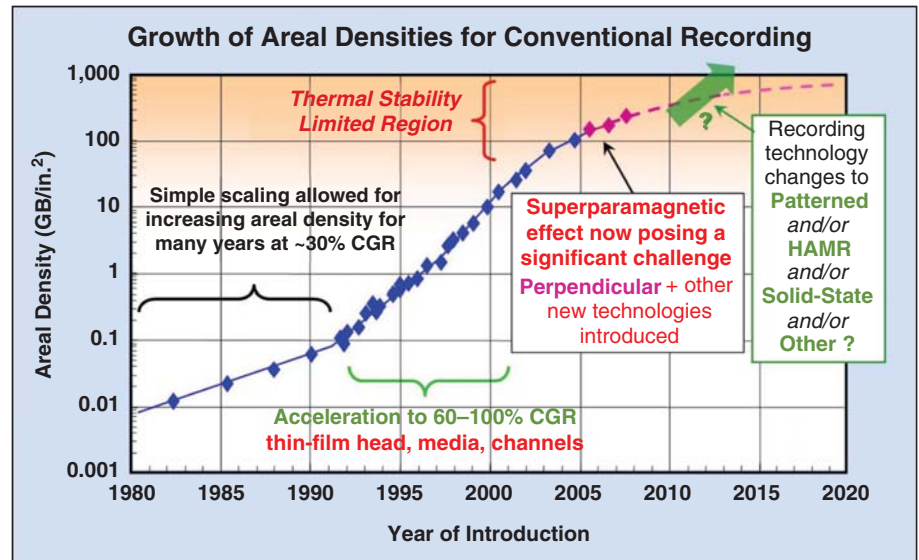


Figure 1. Progress in bit areal density in magnetic hard-disk drives. The acceleration to 60–100% compound growth rate (CGR) in the period from 1992 to 2000 was achieved by advances in thin-film magnetic recording media, reducing the sizes of magnetic recording heads and improving read channels. In the period after 2010, the introduction of new technologies such as patterned media or heat-assisted magnetic recording (HAMR) is expected to enable continuation of the bit areal density.

how they have enabled continued scaling toward higher capacity memories over time. In the case of patterned media (Figure 2a), one bit that contains many exchange-decoupled grains is replaced by a single magnetic island composed of magnetically exchange-coupled material. The size of the island can be as small as 3 nm for FePt, well beyond the superparamagnetic limit. These islands can be packed in bit cells as small as 6 nm × 6 nm, reaching areal densities as high as 15–20 terabits/in.². In the case of crosspoint memories (Figure 2b), silicon-based transistors are replaced with ferroelectric materials, phase-change materials, or magnetic tunnel junctions, to name a few of the proposed alternatives to address the difficulty of scaling silicon-based flash memory. For example, phase-change materials are shown to be scalable down to a cross section of 3 nm × 20 nm.⁵

The scaling challenges of conventional technologies are circumvented by the smart choice of new nanostructured materials, which come at the expense of challenging processing and fabrication. For example, efficient fabrication of patterned media disks requires high-resolution electron-beam lithography tools with rotational stages for the fabrication of masters and nanoimprinting lithography for the cost-effective replication of master patterns onto disk substrates.^{6–8} Additionally, self-assembly or template-guided self-assembly is likely to be required for patterns with critical dimension features smaller than 25

nm.⁸ Proximity effects and long electron-beam writing times make electron-beam lithography impractical at such small critical dimension sizes. Nanofabrication of crosspoint memories will likely require the same approach based on high-resolution low-throughput electron-beam lithography for imprinting masters and low-cost high-throughput nanoimprinting lithography for final device fabrication.⁷

Biological systems might hold the key to a paradigm shift in storage and ultimate nanoscale engineering that can enable future memory scaling. Either DNA⁹ or proteins¹⁰ could be used. For example, it might be possible to encode digital signals or data using DNA in its double-stranded form, which is stable, compact, and inexpensive.⁹ The data can be duplicated using polymer chain recombination and queried using DNA annealing and pairing processes.⁹ One interesting feature of such a system is that the querying time is not dependent on the size of the database, unlike its digital counterpart. DNA kinetics is dependent only on relative concentrations and not the number of different molecules.⁹

In this issue, we have collected state-of-the-art reviews that demonstrate how nanostructured materials engineering drives information storage and enables future growth in areal density and memory capacity for nonvolatile memories. We address key technologies such as hard-disk drives and solid-state memories, as well as

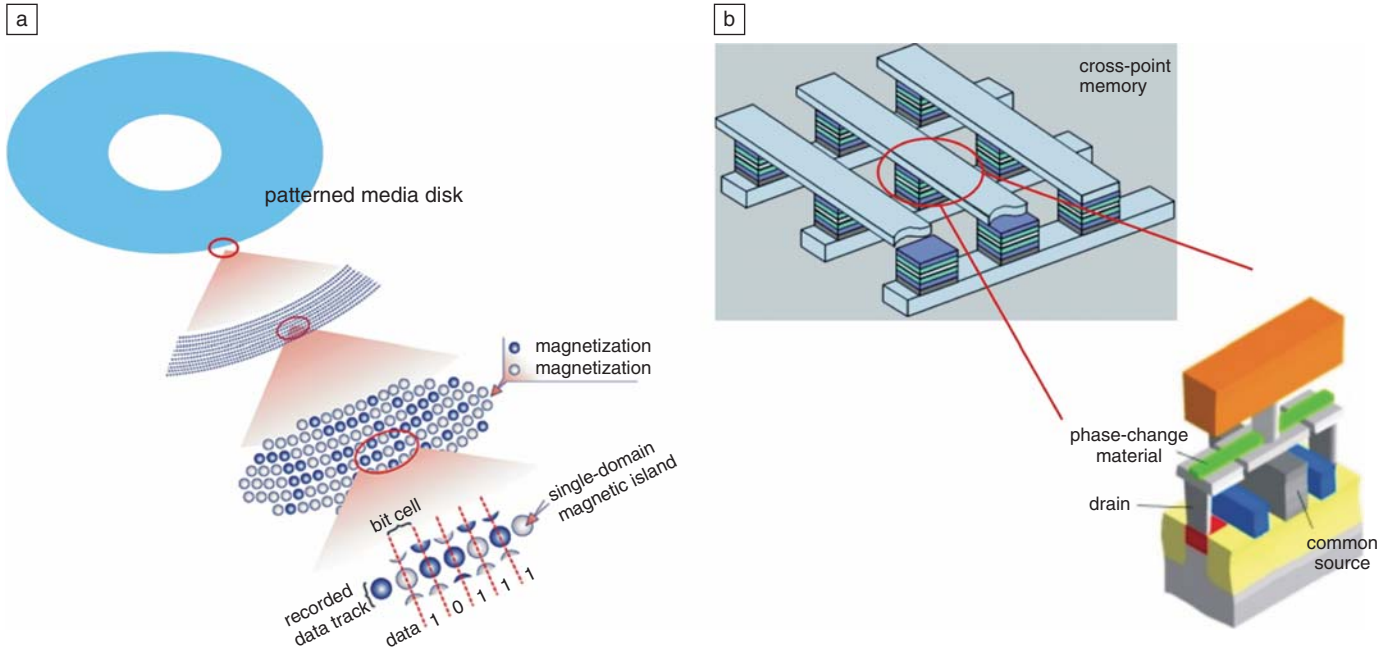


Figure 2. (a) Schematic overview of patterned media disk. Tracks contain an array of prepatterned magnetic islands, and each island consists of magnetic exchange-coupled material that behaves as a single magnetic entity storing one bit of information. (b) Schematic overview of crosspoint memory,⁵ with a non-silicon-based material located at the crossing point. Many materials have been proposed for crosspoint memories, including phase-change materials (shown in the inset), ferroelectric materials, and magnetic tunnel junctions.

nanofabrication methods such as nanoimprinting lithography and self-assembly, as applied to information storage.

Caroline Ross from the Massachusetts Institute of Technology and J.Y. Cheng from IBM Almaden Research describe block-copolymer lithographic fabrication of patterned media. As modern electron-beam lithography tools reach their limit at resolutions beyond critical dimensions of 25 nm, self-assembly-based patterning will likely be required for scalable fabrication of patterned media (and crosspoint memories). Block copolymers that phase-separate into ordered periodic nanoscale structures provide a path to such patterning. Ross and Cheng discuss topographic and chemical patterning of the surface required to introduce long-range order into patterns, pattern transfer into magnetic materials, properties of block-copolymer patterned media, and finally pattern placement uniformity and accuracy.

Simone Raoux, Charles T. Rettner, and Geoffrey W. Burr from IBM Almaden Research and Yi-Chou Chen from Macronix International focus on phase-change random-access memory. A series of time-resolved x-ray diffraction experiments was used to measure large arrays of phase-change nanoparticles of various materials fabricated by electron-beam lithography or self-assembly and to examine the associated phase transitions. All

nanoparticle arrays (with particle sizes varying between 20 nm and 80 nm) exhibited clear evidence of crystallization temperatures similar to those of thick films. Electron-beam-lithography-based techniques were used to fabricate prototype “phase-change bridge” phase-change random access memory devices and to measure their current-voltage and switching characteristics. Raoux et al. demonstrate that devices with cross sections as small as 3 nm × 20 nm still have the expected threshold switching behavior.

Sanjay V. Sreenivasan from the University of Texas at Austin and Molecular Imprints, Inc., who has made major contributions in nanoscale fabrication using imprint lithography, reviews state-of-the-art nanoscale manufacturing opportunities enabled by nanoimprinting. Sreenivasan reviews representative nanoscale devices, namely, patterned media, silicon-based integrated circuits, and photonic crystals. The article discusses the nanofabrication requirements of the devices and the three key building blocks of nanoimprinting: nanoimprinting masks, resists, and tools. Finally, a comprehensive overview follows on resolution, critical dimension control, alignment, overlay, template lifetime, cost, and throughput, ending with a discussion of future directions.

Next, biological-material-based information storage systems are reviewed by

Sakhrat Khizroev from the University of California–Riverside and co-authors. The authors discuss an exciting protein-based recording system and its potential application in the form of a hard-disk drive. They focus on bacteriodopsin (BR) protein and discuss the photocycle of BR, in particular, the core photocycle and “branched photocycle” at room temperature. The article explains how this material can be applied to two-dimensional BR-protein-based information storage systems. Khizroev et al. discuss two-step writing and reading mechanisms for such a system and outline key challenges in optically based write and read transducers. Solutions for power loss in the near-field optical regime are addressed by nanoscale apertures (fabricated by focused-ion-beam lithography), capable of focusing up to 250 nW into a 30-nm spot. The authors also describe a spinstand-based laboratory setup for studying protein-based disk recording.

In this issue of *MRS Bulletin*, we have sought to cover areas of materials science and engineering research that are key enablers for future increases in the density and capacity of nonvolatile memory. From patterned media to phase-change memory, from block-copolymer self-assembly to nanoimprinting lithography, and all the way to biologically inspired information storage systems, we introduce the span of

novel nanostructured systems for memory devices. These systems are capable of high areal densities and high capacities required to bridge the gap to an information-rich and storage-hungry future.

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Society (MRS) conferences, Electrochemical Society meetings, and Cambridge University, Harvard University, and the Max Planck Institute for Polymer Research in Mainz, Germany. In November 2006, he organized an MRS symposium on "Nanostructured and Patterned Materials in Information Storage," which had over 100 oral and poster presentations and was attended by over 200 participants. He was an editor of MRS conference proceedings on nanostructured materials in information storage, and is currently editing a special issue of the IEEE conference proceedings on advances in magnetic storage. In his free time, Bandić plays classical guitar and violin.

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Haddon's research interests have been directed toward the electronic structure and properties of molecules and materials, with particular emphasis on transport, magnetism, superconductivity, device fabrication, nanotechnology, and the discovery of new



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classes of electronic materials. Since entering academia, his research group has turned their attention to the study of radical conductors and carbon nanotubes. In 1998, they prepared the first soluble single-walled carbon nanotubes, allowing the study of carbon metals and semiconductors in solution. Both ionic and covalent solution phase chemistry were demonstrated, with concomitant modulation of the electronic band structure. In 2003, the group turned their attention to quality control in carbon nanotubes and the applications of these materials in biology, composites, sensors, spintronics, and nanoelectronics. Haddon was named 1991 Person of the Year by *Superconductor Week*, and a Fellow of the American Association for the Advancement of Science and the American Physical Society, "for work on organic electronic materials, including the prediction and discovery of superconductivity in alkali-metal-doped carbon-60." He is the recipient of the James C. McGroddy Prize for new materials from the American Physical Society.

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organizer of the IEEE conference on Nanoscale Devices and System Integration and the North American Perpendicular Magnetic Recording Conference. Khizroev has served as associate editor for *IEEE Transactions on Nanotechnology*, and as a guest editor for *Nanotechnology* and *IEEE Transactions on Magnetics*. His current research focus is in the sub-area of nanotechnology, dedicated to the development of nanomagnetic technologies for information, medicine, and energy-harvesting related applications. Khizroev has over 26 granted, nine pending, and 110 provisional patents with IBM, Seagate, CMU, FIU, and UCR. He has also authored/co-authored over 80 refereed papers, and five books and book chapters.

Simone Raoux is a research staff member at the IBM Almaden Research Center. She received her MS degree in 1984 and her PhD degree in physics in 1988, both from Humboldt University, Berlin. From 1988 through 1991, she worked as a staff scientist at the Institute for Electron Physics in Berlin. From 1992 through 2000, Raoux was a staff scientist at



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Rettner joined IBM Research in 1983 after postdoctoral studies in the chemistry departments of the Massachusetts Institute of Technology in 1979 and Stanford University from 1980 through 1983. Until the mid 1990s, his research was mainly concerned with the dynamics of chemical reactions, especially those at surfaces. In recent years, he has worked more on

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