Phase-change recording medium that enables ultrahigh-density electron-beam data storage

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An ultrahigh-density electron-beam-based data storage medium is described that consists of a diode formed by growing an InSe/GaSe phase-change bilayer film epitaxially on silicon. Bits are recorded as amorphous regions in the InSe layer and are detected via the current induced in the diode by a scanned electron beam. This signal current is modulated by differences in the electrical properties of the amorphous and crystalline states. The success of this recording scheme results from the remarkable ability of layered III-VI materials, such as InSe, to maintain useful electrical properties at their surfaces after repeated cycles of amorphization and recrystallization. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1856690]

Inspired by a growing demand for high-density data storage, researchers have proposed scanned probe memories based on topographic transformation,[1–3] conductance modification,[4–6] ferroelectric polarization,[7] charge storage,[8,9] changes of phase,[10] and near-field optical recording.[11,12] The devices proposed to date have suffered from limited data rates, inadequate signals, or high cost. We have developed a viable storage device that provides large signals at high data rates from nanoscale bits. This device consists of three components: A microfabricated array of field-emitting electron sources used to read and write bits, a diode medium with a phase-changeable data storage layer, and a micromachined *xy* stage capable of translating the storage medium with subnanometer precision. This letter describes the storage medium, which provides a means to circumvent the optical diffraction limit and transform the phase-change technology that forms the basis for rewriteable optical recording.

As shown schematically in Fig. 1, the storage medium consists of InSe grown epitaxially on Si(111) with a thin intermediate buffer layer of GaSe (for growth methods see EPAPS Ref. 13). InSe and GaSe are *n*- and *p*-type semiconductors, respectively. When deposited on *p*-type silicon, these layers form a rectifying device (EPAPS supplementary text and Fig. S1, see EPAPS Ref. 13). Like the Te-based chalcogenides used in rewritable optical recording, InSe can be reversibly switched between the crystalline and amorphous states.[14] To write an amorphous bit, a high-power electron or optical beam is used to melt-quench a small region at the surface of the InSe. For erasure, a lower power beam heats a bit above its crystallization temperature. To read data back, the beam is scanned over the surface at a power-density insufficient to cause erasure and generates electron-hole pairs within the InSe. The *pn*-junction diode formed by the chalcogenide layers and silicon substrate is reverse-biased so that the generated minority carriers are swept across the junction, creating a current that constitutes the readout signal. The minority carriers' mobility is low in amorphous regions, and their lifetime is short due to the high density of recombination sites. Consequently, when the beam is incident on an amorphous bit, the efficiency with which the generated carriers are "collected" is low, providing contrast in the signal current.

This readback mechanism enables large signals from nanoscale bits because an electron of energy E_0 impinging on a semiconductor with band gap E_g creates approximately $E_0/(2.1E_g+1.3)$ electron-hole pairs (energies measured in electron volts).[15] Thus, even small minority-carrier collection efficiencies can result in induced diode currents many times larger than the interrogating beam current. This gain makes possible signal-to-noise ratios that allow a readback data rate in excess of 1 MHz/emitter. Thousands of microfabricated emitters can be incorporated in a single $1\ \mathrm{cm}\times 1\ \mathrm{cm} \times 1\ \mathrm{mm}$ module[16] resulting in overall data rates greater than one gigabit/s.

InSe and GaSe consist of sheets comprised of four atomic planes in the sequence Se–M–M–Se (M=Ga or In) (EPAPS Fig. S2, see EPAPS Ref. 13). Strong ionocovalent bonds connect the atoms within a sheet, but there are only

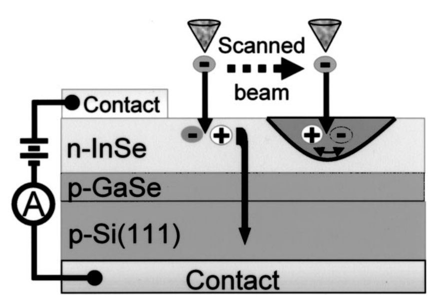

FIG. 1. Schematic of phase-change diode storage medium. An electron beam is scanned over the surface of the diode and generates electron-hole pairs. The minority carriers are swept across the diode and cause a readout current to flow in an external circuit (labeled A). When the beam is incident on an amorphized region, the signal current is smaller because most of the generated carriers rapidly recombine.

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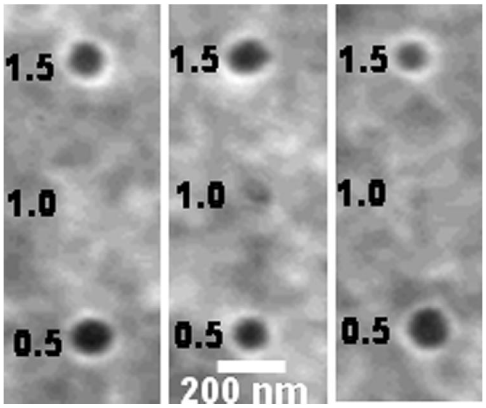

FIG. 2. Maps of the current induced across an InSe(100 nm)/GaSe(10 nm)/*p*-Si(111) diode by a 1.5 keV, 5 nA electron beam. The bits labeled "0.5" are amorphous marks written in the InSe layer using a 5.6 mW, 30 ns laser pulse. The bits labeled "1.0" have undergone a single write/erase cycle consisting of a 5.6 mW, 30 ns amorphizing pulse followed by a 1.8 mW, 1 ms recrystallizing pulse. The bits labeled "1.5" were reamorphized using an additional 5.1 mW, 30 ns laser pulse. The induced current has been restored to nearly its original level in the recrystallized bits.

weak van der Waals attractions between the Se planes that bound each four-plane unit.[17] This highly anisotropic bonding makes InSe/GaSe/Si(111) epitaxy possible despite large lattice mismatches.[17] Cross-sectional transmission electron microscope (TEM) images show that the crystalline quality of our films is excellent.[18] Most importantly, the anisotropic bonding of the layered compounds results in Se-terminated surfaces that lack recombination-inducing dangling bonds and do not exhibit problematic surface reconstructions, dipoles, or band bending.[17] These features permit a high collection efficiency for minority carriers generated near the InSe surface. A signal gain (induced diode current/incident beam current) as large as 15 is obtained at an electron-beam energy of only 700 eV from an epitaxial InSe(50 nm)/GaSe(5 nm)/Si(111) stack. A simple estimate (EPAPS supplementary text, EPAPS Ref. 13) indicates that this gain represents a collection efficiency of well over 10%. Such a high collection efficiency is remarkable given that a sub-keV electron beam generates carriers within a few nanometers of the surface,[19] where they are highly susceptible to recombination. A reasonable gain at sub-keV energies is critical to the success of the data storage device because higher beam energies require prohibitively large power supplies and can cause dielectric breakdown of device components. The observed high collection efficiency indicates not only that recombination at the InSe surface is reasonably slow, but also that there are no problematic interfacial band offsets and that the chalcogenide films have an adequate mobility-lifetime product for minority carriers. The InSe/GaSe/Si(111) devices exhibit other requisite electrical properties, such as a low reverse bias leakage (dark) current (EPAPS Fig. S1, see EPAPS Ref. 13). High reverse-bias leakage currents would lead to unacceptably high power requirements and noise in the readback signal.

Figure 2 displays signal maps created by rastering the electron beam of a scanning electron microscope over a diode area containing laser-cycled bits of 150–200 nm diameter and ~20–40 nm depth. The grayscale is proportional to the diode current induced by a 1.5 keV, 5 nA electron beam. A laser was used to create these bits because currently available electron-beam sources do not have the power density

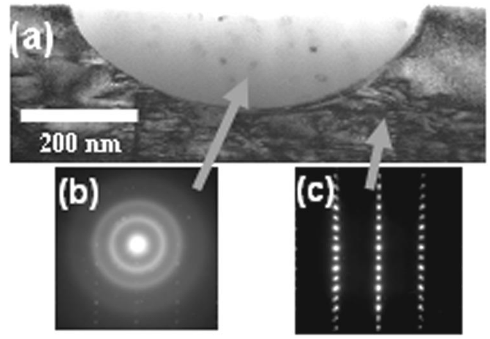

FIG. 3. (a) TEM cross section of a laser-written amorphous bit created in an epitaxial InSe film. (b) Rings in the selected-area diffraction pattern verify that the bit is amorphous. (c) The two sets of (00l) diffraction spots indicate that the InSe and GaSe are epitaxial.

needed to melt submicron regions of InSe. The low thermal conductivity[20] and 660 °C melting point of InSe should make it possible to melt the InSe with electron beams of achievable power density in the near future. InSe's crystallization temperature of ~300 °C is nonetheless sufficiently high to make amorphous bits stable near room temperature (EPAPS supplementary text, see EPAPS Ref. 13).

The signal is almost completely quenched over the amorphous bits of Fig. 2, thereby providing strong contrast in the readout signal (see discussion in EPAPS supplementary text and Fig. S4, EPAPS Ref. 13). Surprisingly, the annealed bits show nearly complete restoration of the collection efficiency. TEM data on *in situ* electron-beam-annealed bits suggest that they regrow from the surrounding crystalline matrix rather than forming randomly oriented grains at nucleation sites within the amorphous region (EPAPS Fig. S3, see EPAPS Ref. 13). Therefore, the unmelted regions appear to act as a template for epitaxial regrowth of InSe with a low density of recombinative defects and a minority-carrier mobility comparable to that of the original epitaxial layer.

Complete restoration of the signal upon erasure is critical because, for many data storage applications, the collection efficiency of the crystalline state must still be high after many thousands of write/erase cycles. Thus, melting the phase-change material must not cause phase-segregation, ablation, reaction with the environment, or diffusion across the *pn*-junction. Figure 3 shows a cross-sectional TEM image of a laser-written amorphous bit in an epitaxial InSe layer. Electron diffraction patterns from such bits confirm that melt quenching has left the InSe amorphous. TEM-based energy dispersive x-ray measurements find no evidence for compositional changes within or near these bits. Any material losses are not large enough to show up as thickness changes in plan-view atomic force microscope or cross-sectional TEM images.

To date, we have toggled the diode signal through more than 100 laser write and erase cycles. After 100 cycles, the contrast between the written and erased states drops by nearly 50% due to a decrease in signal from the recrystallized state. Possible explanations for this degradation include gradual changes in composition and accumulation of structural defects. Future optimization of write-erase parameters should reduce this degradation. Capping layers consisting of a few nm of molybdenum and SiO_2 significantly improve the ability of the storage medium to withstand write-erase cycling but they also decrease the signal by attenuating the electron beam (EPAPS supplementary text and Fig. S5, see EPAPS Ref. 13).

The most important remaining issue in demonstrating the feasibility of the electron-beam-addressed phase-change storage medium is to show that the read mechanism provides a sufficiently large signal-to-noise ratio for sub-150 nm diameter bits. Minority carriers may escape from very small amorphous bits before recombining, thereby reducing contrast. Also, closely spaced amorphous bits may diminish the signal from neighboring crystalline regions. Future work will concentrate on studying these issues in smaller diameter bits created with high power density electron beams. It should be noted that bit depth is highly dependent on the thickness of the chalcogenide layers because their thermal conductivity is approximately two orders of magnitude lower than that of the silicon substrate. Thermal modeling shows that an electron beam can create sub-30 nm diameter bits that will be nearly as deep as laser-written bits that have already demonstrated excellent signal contrast.

In summary, the electrically benign properties of the chalcogen-terminated surfaces of InSe and GaSe allow fabrication of diodes with high minority-carrier collection efficiencies within nanometers of their top surface. These layers grow epitaxially on silicon, making the overall device amenable to low-cost manufacture. Using these devices, we have demonstrated that 150 nm diameter amorphous bits written in the InSe provide strong contrast in the electron-beam-induced diode current. To date, we have amorphized and recrystallized individual bits 100 times while retaining the electrical properties necessary to provide a high carrier collection efficiency in the crystalline state. The remarkable ability of InSe to repeatedly recrystallize with high carrier mobilities and lifetimes appears to result from its tendency to regrow epitaxially from the surrounding crystalline matrix with minimal compositional and structural defects. These results establish the feasibility of using phase-change media for ultrahigh density, electron-beam-based data recording.

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