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Reading data stored in the state of metastable defects in silicon using band-band photoluminescence: Proof of concept and physical limits to the data storage density

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The state of bistable defects in crystalline silicon such as iron-boron pairs or the boron-oxygen defect can be changed at room temperature. In this letter, we experimentally demonstrate that the chemical state of a group of defects can be changed to represent a bit of information. The state can then be read without direct contact via the intensity of the emitted band-band photoluminescence signal of the group of defects, via their impact on the carrier lifetime. The theoretical limit of the information density is then computed. The information density is shown to be low for two-dimensional storage but significant for three-dimensional data storage. Finally, we compute the maximum storage capacity as a function of the lower limit of the photoluminescence detector sensitivity. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4870002]

In order to overcome the limits of current hard drives, numerous technologies have been recently proposed.[1–3] The most advanced storage technologies, already at the product stage,[1,4,5] include storage in the polarity of magnets (Magnetic MRAM), in the ferroelectric properties of materials (Ferroelectric FeRAM) and in the heat-induced change of a material phase (Phase Change PCRAM). Some are at an earlier stage of research and include memory using the conductivity of materials (Resistive RRAM) or in the spin of electrons (Spin Transfer Torque STTRAM).[1,2] These new technologies address the need for fast access time (reading and writing), small cell size, high endurance, and high power efficiency required by the cache and the main memory. However, they do not address the low cost, low power usage, and long retention time required for persistent storage and data archiving (a role currently fulfilled by magnetic disks and flash memory).

One of the most promising technologies for such data archiving with high retention times are volumetric optical data storage.[6] Two approaches are taken for optical data storage, one where each bit of data is assigned a specific location (localized data storage) and the other where the information is distributed through a volume (delocalized data storage). Holographic memory is the main form of delocalized optical data storage.[2,6,7] Localized optical data storage have been achieved by refractive changes in photochromic and photorefractive materials, mainly polymers, the reading being done through transmission, reflection, fluorescence, or photoluminescence based methods.[6] In this paper, a potential new medium and method for low cost and long term localized optical data archiving is introduced.

We demonstrate a method to store the bit of information in the state of metastable defects in crystalline silicon and read the states of the defect through their band-band photoluminescence emission. Metastable defects have been suggested before for optical data storage, for example, metastable defects have been used in GaAs to change the conductivity of the material,[8] and hence the optical transmission. Photoluminescence has also been used for reading information stored in different media, for example, in vitreous silica.[9,10] However, the combination of silicon metastable defects and band-band photoluminescence has not been demonstrated as a potential data storage method.

Iron possesses a positive charge and is thus paired with negatively charged boron in p-type silicon.[11] Upon illumination and creating electron-hole pairs, iron-boron pairs can be broken with the interstitial iron atom diffusing away from the substitutional boron. The two configurations, interstitial iron, and iron-boron pairs, lead to two different recombination activities, which can be observed from the intensity of the band-band photoluminescence under illumination.[12–14] By selectively and spatially changing the state of metastable iron-boron pairs, one can thus store information in the silicon and read the state of the metastable defects through their band-band photoluminescence signal. Note that interstitial iron is not stable[11] at room temperature (typical repairing times are in the order of 10 min depending on the sample doping) so other metastable defects such as the boron-oxygen defect may be more suited for long term stability.[15] However, their properties are better known; and hence, they are useful for a proof of concept.

The sample used in this study was a 490 μm thick Float Zone (FZ) p-type monocrystalline silicon wafer. The sample was etched and phosphorus-diffusion gettered (880 °C, 1 h). Although FZ silicon is usually highly pure, this step effectively removes fast diffusing metallic impurities potentially present in the material. The diffused region was subsequently etched away. The sample was then implanted with 70 keV Fe^{56} ions to a dose of 5×10^{11} cm^{-2} on one surface. The sample was annealed at 900 °C for 1 h in order to obtain a maximum volume concentration (corresponding to the solubility limit) of iron of 4.3×10^{13} cm^{-3} in the bulk of the material (measured concentration 8×10^{12} cm^{-3}). The sample was then etched and surface-passivated using Plasma-Enhanced Chemical Vapor Deposited (PECVD) silicon nitride deposited at 400 °C. Metastable defects were then activated

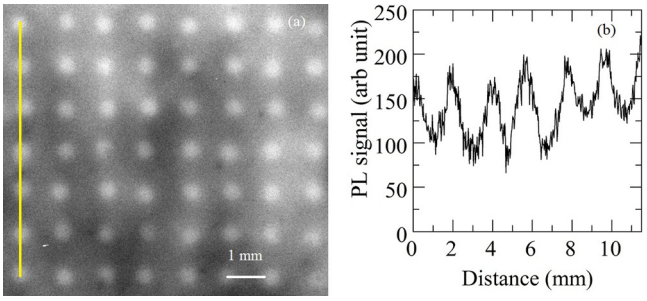

FIG. 1. (a) 195 bits of data (alternating 10101 and 00000 sequence with every bit 1 mm in size) written in a monocrystalline silicon sample of doping $2.8 \times 10^{15}\,\mathrm{cm}^{-3}$ and $\mathrm{Fe} = 8 \times 10^{12}\,\mathrm{cm}^{-3}$ (b) profile of the measured PL signal showing the strong contrast between activated and inactivated regions.

selectively using a flash of light through an aperture mask representing the information to be written. The sample was measured using a commercially available photoluminescence imaging tool.[16]

Figure 1(a) shows the photoluminescence signal (Figure 1(b) shows a profile of the signal) of the silicon sample, where the metastable defects have been previously activated selectively. The pattern is a series of alternating 01010 and 00000 sequences with every bit approximately 1 mm wide, making up a total of 195 bits of data. The regions where the pairs have been broken appear as brighter regions, with higher band-band luminescence. One can clearly see that not only binary states can potentially be written using these defects but also multiple-value states. The profile of the writing excitation is square; however, Figure 1(b) shows that the PL signal read from the sample is not sharp at the edges of the bits. This is partly due to carrier smearing (diffusion of minority carriers laterally in the samples due to a relatively high diffusion lengths of 40 μm) both during the creation of the pattern and during the reading of the pattern. Note that photon spreading in the CCD detector can also account for the apparent smearing of the signal; however, we did not see a significant change of the signal after applying a deconvolution procedure.[17]

From above it is clear that without considering the detector sensitivity, it is the diffusion length (as opposed to the inter defect distance, which is several orders of magnitude smaller) which dictates the bit size. There are three parameters one can change in principle to reduce the diffusion length: the defect density, the doping density, and the number of electron-pairs created during reading (the excess carrier density). Figure 2(a) shows that one cannot reduce the diffusion length very much below 1 μm. This limit is imposed by the maximum practical solubility of iron in silicon ($[\mathrm{Fe}] = 2.45 \times 10^{16}\,\mathrm{cm}^{-3}$ at 1200 °C). Increasing the doping density (Figure 2(b)) can further reduce the diffusion length through a reduction of the minority carrier mobility; however, the effect is minor. Increasing the excess carrier density (Figure 2(c)) during reading leads to a constant diffusion length, and an increase of the diffusion length for high excess carrier density. This is due to the fact that at high carrier concentration the minority carrier lifetime limited by interstitial iron increases with carrier injection.[18]

A bit size of 1 $\mu\mathrm{m}^2$ would not be competitive with current storage technologies which are already several orders of magnitude smaller, down to 1000 nm^2,[1] or more recent technologies (MRAM, FeRAM, and PCRAM), which have bit sizes between 1 $\mu\mathrm{m}^2$ and 0.01 $\mu\mathrm{m}^2$.[1] However, as light is used to both write and read the state of the metastable defects, one can potentially write and read the data in three dimensions, similarly to common optical storage.[6,7] Note that contrary to photorefractive based optical storage and holographic storage, where the reading is done purely optically, here, the data are stored electronically and read through activation of certain bits and reading of the corresponding photoluminescence signal (as in fluorescence based storage). One could imagine using multiple infrared lasers to write and read the data inside a cube of silicon (note that as an infrared laser would be used, the maximum beam size would be capped by the wavelength of the laser 1.2 μm, which is very similar to the bit size). However, there will be a limit to the volume of silicon that can be used for such storage, as emitted photons will be weakly re-absorbed by the silicon crystal. The maximum storage volume will thus depend on the photoluminescence detector sensitivity. Figure 3 shows the maximum storage achievable and length of the storage cube as a function of the minimum photon flux detectable by the detector. For this simulation, we used binary states and assumed that a bit is 3 times larger than the diffusion length. With a corresponding data density of 0.01 bits $\mu\mathrm{m}^{-3}$, this also ensures we are not limited by the optics which sets the maximum achievable data density at 0.69 bits $\mu\mathrm{m}^{-3}$ (corresponding to $1/\lambda^3$ with $\lambda = 1.2\,\mu$m). We also assume that an excess carrier concentration of $\Delta n = 1 \times 10^{14}\,\mathrm{cm}^{-3}$ can be created locally in the volume. As the storage volume gets larger, this can be achieved by shifting the wavelength of the reading laser beam towards higher wavelength (and increasing the intensity). The results show that, for instance, a cube of 8.3 cm^3 has the capacity to store 1.02 TB (8.13 TBits) of information provided that the

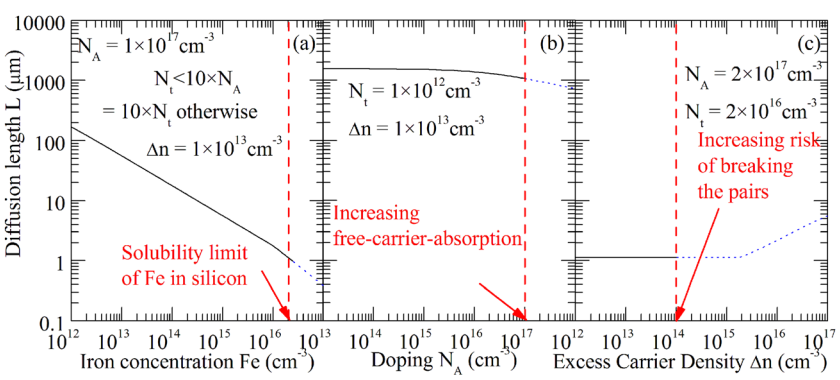

FIG. 2. Diffusion length of minority carriers as a function of (a) interstitial iron concentration, (b) dopant concentration, and (c) excess carrier density during measurement. Practical limits for each of the parameters are also included.

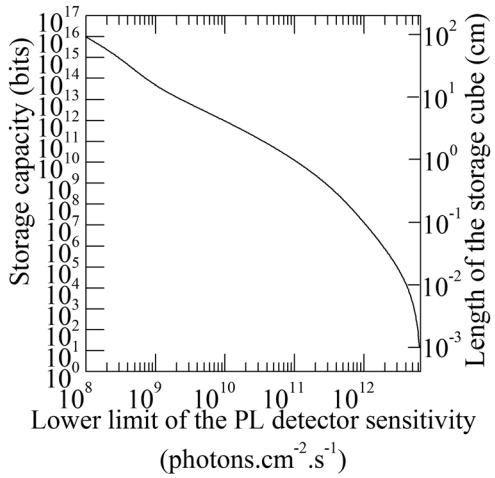

FIG. 3. Maximum storage capacity and maximum length of the storage cube as a function of the lower limit of the detector sensitivity for 3-dimensional storage. The size of the 3 dimensional storage is limited by re-absorption of the photoluminescence.

detector can detect photon fluxes as low as 9.5×10^9 photons $cm^{-2}\ s^{-1}$.

We have demonstrated that a bit of information can be written in the state of metastable defects in silicon. The state of the defect and hence the information can then be read by the local photoluminescence intensity. With a potential bit size of 1 μm^2 this technology is not competitive with current two dimensional storage technologies. One could, in principle, decrease the bit size further by incorporating super-saturated concentrations of impurities, for example, through liquid state recrystallization of laser annealed iron coated silicon surfaces. Moreover, this technology could be scalable in three dimension as it does not require contacting each of the bits (in contrast to current three dimensional storage such as 3D NAND and hybrid memory cells, which require complex 3 dimensional electronic interconnections), as it uses light to both write and read the information. The defect used in this study is not stable, meaning that the iron will repair with boron atoms over time scales of minutes. However, one could potentially use other light sensitive and stable defects such as the boron-oxygen defect. Finally, the technology could be used to store binary states as well as multiple-value states, depending on the lower limit of the detector sensitivity.

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