Thin-Film Carbon Nanofuses for Permanent Data Storage

Kevin R. Laughlin,† Sarah Jamieson,‡ Anthony C. Pearson,† Hao Wang,‡ Richard R. Vanfleet,† Robert C. Davis,§,†‡ Sarah Jamieson,† Anthony C. Pearson,‡ Hao Wang,‡ Richard R. Vanfleet,† Robert C. Davis,§,†‡ Matthew L. Linford,§ and Barry M. Lunt§

1Department of Physics and Astronomy, N215, 2Department of Chemistry and Biochemistry, C389 BNSN, and 3School of Technology, 265 CTB, Brigham Young University, Provo, Utah 84602, United States

ABSTRACT: In this study, we have fabricated nanofuses from thin-film, arc-deposited carbon for use in permanent data storage. Thin-film carbon fuses have fewer fabrication barriers and retain the required resistivity and structural stability to act as a data-storage medium. Carbon thin films were characterized for their electrical, microstructural, and chemical bonding properties. Annealing these films in an argon environment at 400 °C reduced the resistivity from about $4 \times 10^2$ Ω cm as deposited to about $5 \times 10^{-2}$ Ω cm, allowing a lower blowing voltage. Nanofuses with widths ranging from 200 to 60 nm were fabricated and tested. They blow with voltages between 2 and 5.5 V, and the nanofuses remain stable in both “1” and “0” states under a constantly applied read voltage of 1 V for over 90 h.

INTRODUCTION

In just over 60 years, from 1951 to 2013, the amount of data that can be stored digitally on a single data-storage device has increased from 224 kB to 88 TB. Unfortunately, to achieve these high data densities, the mean lifetime of the stored data has been sacrificed. As a result, digital data-storage devices, such as digital video disks (DVDs), hard drives, and flash memory, have a mean lifetime of less than 10 years. Possible failure mechanisms of these devices can include atomic diffusion, electromigration, oxidation, and other chemical changes (Figure 1). To reliably maintain data for more than 10 years, multiple copies are made and the data are periodically migrated. However, these solutions are time consuming, involve additional expenses, require complex systems for large data volumes, and can still result in data loss.

Permanent data-storage media require long-term stability of both “1” and “0” states of the data. For example, a comparison of conventional and permanent data-storage media for optical and solid-state devices is illustrated in Figure 1. Writable compact disks and DVDs contain organic dyes with limited long-term stability. The M-disc, used for permanent data storage, by contrast, uses structural changes in an inorganic layer to store the data (Figure 1D). This results in data stability of more than 1000 years.

Solid-state flash memory has become widely used for a variety of reasons, including its convenient form factor, low power requirement, lack of moving parts, and much higher read/write speeds than optical and magnetic disks. Flash-based solid-state data-storage works by storing charge on a floating gate in a transistor. To write a data bit in flash memory, charge is injected onto the floating gate through a thin insulating layer. However, over a time scale of years, a significant amount of the charge that is stored on the floating gate will tunnel out through the insulator, resulting in data instability and loss (Figure 1). For the development of permanent solid-state data storage, there is a need to transition from charge-based and reversible phase change media to irreversible, structurally based storage mechanisms. These mechanisms could include irreversible phase changes, stable chemical bonding changes, or material displacement. Structurally based data storage using microscale metal fuses was prevalent from the 1970s to the 1980s. These metal fuses (Figure 1) were the basis for programmable read-only memory. An intact fuse allows current to flow, whereas a blown fuse does not allow it, corresponding to data bits of 1 and 0, respectively. At the blowing voltage, the metal in the fuse melts and is displaced, opening up an insulating structural gap. Even though metal fuses use a structural change to store data, the high surface mobility of the metal allows atoms to migrate when a voltage is applied over time. This caused fuses to exhibit dendritic growth in the blown state, forming conductive paths across the fuse gap and resulting in data corruption.

In contrast to metals, conductive graphitic carbon has high structural stability because of its much higher localized bond strength. Graphene is an atomically thin sheet of graphitic carbon, which does not readily oxidize below 300 °C and has thermal and electrical resistivities that could allow fuses to write in the single-volts range. Graphene has recently been used to create carbon fuses, where a write voltage permanently oxidized the fuse, resulting in a stable structural gap. Consistent with carbon’s high local bonding strength, these graphene fuses do
not demonstrate dendritic growth. These graphene fuses were fabricated from chemical vapor deposition (CVD)-grown graphene films. CVD-grown graphene layers are polycrystalline, containing grain boundary and other defects and requiring transfer to an insulating substrate. The grain boundaries, defects, and transfer-induced damage of the delicate graphene sheets result in significant barriers to manufacturing. In short, fabrication of high-performance electronic devices with graphene is an active area of research, but there is currently no industrial electronic device manufacturing from graphene due to the significant quality and cost barriers. Conversely, physical vapor deposition (PVD) of carbon is widely used industrially and consequently can be much more readily integrated into current electronic manufacturing.

Thin-film carbon can be deposited by widely used PVD processes, including sputtering, electron-beam deposition, and arc deposition. Sputtered carbon thin films have resistivities of approximately $10^4 \, \Omega \, \text{cm}$, whereas arc-deposited and e-beam-evaporated carbon thin films have significantly lower as-deposited resistivities, in the range of $10^{-2} \, \Omega \, \text{cm}$, which can be further lowered by annealing. Using the relationship between temperature, thermal conductivity, and electrical conductivity, as described by Pearson, a carbon nanofuse will reach the required temperature to be programmed at 3 V if the resistivity is less than $10^{-2} \, \Omega \, \text{cm}$. This means that either arc-deposited or e-beam-evaporated carbon would work for this purpose.

Here, we fabricated nanofuses with arc-deposited carbon, as illustrated in Figure 2. When a programming voltage is applied to the fuse, the thin neck of carbon is heated and oxidized. The oxidation process results in a nonconductive gap (a blown fuse). Blown and unblown fuses represent data bits of 0 and 1, respectively. For this study, over 100 carbon nanofuses were fabricated and tested with carbon thickness, length, and width of 20, 250, and 60–200 nm, respectively.

The PVD-grown carbon represents a significant materials and processing departure from graphene. In contrast to the crystalline monolayer graphene used previously, this PVD-grown carbon is amorphous and 100 times thicker, resulting in significantly different electrical and thermal characteristics. An important question is whether the time required to blow a fuse with this thicker material will be prohibitive; consequently, we measured the data write time and power requirements. The thin-film carbon nanofuses were irreversibly written, with low power requirement between 0.5 and 3.5 mW, and writing speeds of less than 200 ns.

We also studied the voltage and current requirements for fuses with lateral dimensions down to five times smaller than the
These studies provide data that will be valuable in determining the feasibility of obtaining permanent memory from PVD-grown amorphous carbon and the productive fuse geometries.

Decreasing the width of carbon nanofuses also decreases the voltage and power required to blow them. This allows production of fuses that will blow at less than 3 V, which is similar to that of the current flash memory. Just as importantly, when a thin-film carbon nanofuse is blown, dendritic growth is not observed. The stability of these fuses was excellent; no degradation was seen in either the blown or unblown states when tested for a time equivalent to $10^{12}$ reads.

### EXPERIMENTAL SECTION

**Thin-Film Carbon Nanofuse Fabrication.** The nanofuse fabrication process is outlined in Figure 2. The nanofuses were fabricated on a silicon substrate with a 250 nm thick thermal oxide to provide electrical isolation. Gold pads were first made by spinning 950 k PMMA (6 wt %) in anisole (MicroChem) on the substrate at 3000 rpm, which was then placed on a hot plate at 220 °C for 90 s. The PMMA was then exposed with a line dose of 120 μC/cm² using 30 keV electrons from an FEI XL30 ESEM equipped with a high-speed beam blanker. The samples were developed using a methyl isobutyl ketone−isopropanol (MIBK/IPA) 1:3 mixture (MicroChem) for 60 s and then spray-rinsed with acetone for 2 s, followed by a 10 s IPA rinsing. Next, an 80 nm gold layer was thermally deposited at $5 \times 10^{-6}$ Torr, with an evaporation rate of 0.5 Å/s. The carbon rods were sharpened to a cylindrical point, with length and inner width of 5.5 and 1.25 mm, respectively. The sample was finally placed in an acetone bath for 30 min to lift off the excess carbon and rinsed with IPA for 10 s. This resulted in a bow-tie-patterned carbon nanofuse that is electrically connected between two gold contact pads. The bow-tie geometry of the fuse with a narrow neck was chosen because it focuses the current to a small region, allowing the temperature increase to be localized to the center of the fuse. The samples were then annealed in a 1 in. quartz tube heated to 400 °C in an argon environment to decrease the resistivity of the carbon.

### RESULTS AND DISCUSSION

**Thin-Film Carbon Characterization.** To characterize the thin-film carbon, its surface roughness, sheet resistance, microstructure, and the carbon sp²/sp³ ratio were determined. The roughness was measured on a 10 nm layer of carbon (as measured by a calibrated Xtal monitor) deposited on an oxidized, polished silicon wafer. The step height and roughness of the carbon film were measured on a Dimension 3100 atomic force microscope (AFM) in tapping mode. Figure 3A,B shows that the AFM step height of 10 nm matched the target thickness and that the measured roughness of the thin carbon film was 0.53 nm. The sheet resistivity was measured on a 20 nm thick carbon film deposited on a 250 nm thick thermal oxide on a silicon wafer. Four-point probe measurements were then heat-treated on a hot plate at 185 °C for 60 s. A bow-tie geometry was exposed into the electron-beam resist by exposing the patterned area with a line dose of 230−250 μC/cm² using 30 keV electrons. The sample was then spray-rinsed with IPA for 10 s.
yielded a resistivity of 0.041 ± 0.007 Ω cm. Previous studies on arc-deposited carbon have shown that resistivity is reduced by thermal annealing. The impact of annealing in an inert environment at lower temperatures was explored. Specifically, the carbon films were annealed in an argon environment at 400 °C for various times. The effect of annealing time on resistivity is shown in Figure 3C. Annealing the as-deposited carbon layer at 400 °C for 10 min in argon reduced the resistivity by approximately 2 orders of magnitude.

To determine carbon microstructure and bonding, a 10 nm layer of carbon was deposited onto a flat salt crystal. The carbon film was delaminated from the salt crystal by placing it briefly in a water bath and rinsing for 1 h in water. The film was split and placed onto two 300 mesh titanium transmission electron microscopy (TEM) grids and air-dried. One of the carbon samples was annealed for 10 min in an argon environment. To characterize the microstructure, composition, and chemical bonding of the carbon, a Tecnai F20 TEM was used to obtain diffraction patterns, energy-dispersive X-ray spectroscopy (EDX) data, and EELS data. The diffraction pattern showed that the thin-film carbon is amorphous (Figure 3D). The EDX data indicated that the film was composed of carbon with a small amount of silica, which we attribute to the silicone pump oil in the carbon deposition system. On analyzing the EELS results (Figure 3E), a strong sp² peak is visible. We compared the arc-deposited thin film of carbon with sp² standards (lacey carbon film and ultrathin carbon black, Ted Pella product #01824).

**Nanofuse Characterization.** Figure 4 shows scanning electron microscopy (SEM) images of 73 carbon nanofuses with varying sizes as well as their current–voltage (I−V) plots. In the SEM images, the dark bow-tie-shaped region is the carbon fuse. The widths of the middle regions of the fuses vary from 200 to 60 nm. Above and below the fuse, the electrically insulating SiO₂ layer (the lighter region) is visible. Bumps like those on the carbon in Figure 4A were seen on a few devices, which we attribute to residue obtained from the liftoff process. I−V measurements were used to determine the voltage and current required to write to a fuse. For this measurement, a voltage starting at 0 V and increasing at a rate of 0.5 V/s was applied to an intact fuse until the current abruptly dropped to zero, indicating that the fuse had oxidized and was blown. The voltage at which the current dropped to zero is the writing voltage, and the slope of the I−V curve shows the resistance of...
the fuses. For the 200, 150, 100, and 60 nm fuses, the measured writing voltages were 5.1 ± 0.3, 3.3 ± 0.3, 3.0 ± 0.1, and 1.8 ± 0.6 V, respectively. These voltages give a window, where any voltage below would not change the nanofuse, whereas any voltage above would result in a blown fuse.

To measure the time required to write to a carbon nanofuse, a square voltage pulse that was 50% higher than the writing voltage was applied using a Hewlett-Packard 214B pulse generator (refer to Figure 5F for a schematic of the setup). The voltage across a 1 kΩ resistor in series with the carbon nanofuse was used to measure the current passing through the fuse. When the current dropped to zero, the fuse was considered to be blown. To ensure that the nanofuse was blown, a voltage was applied across the nanofuse and no current was measured. The current decay seen in Figure 5F indicates a write time of less than 200 ns.

The electrical read stability of carbon nanofuses was tested by applying a constant read voltage of 1 V (well below the writing voltage) over an intact fuse and monitoring the current over time. To accelerate the testing of blown carbon and metal fuses, a voltage of 10 V (well above the writing voltage) was applied. Figure 6 shows the electrical read stability of carbon nanofuses and the electrical instability of metal nanofuses due to structural degradation. With a bit read time on the order of 100 ns, the 90 h test is equivalent to having a field present for greater than 10¹² reads.

**DISCUSSION**

Significant variation in the writing voltage is unacceptable for a data-storage medium. This voltage variation can come from film roughness, manufacturing imprecision, and grain boundaries. A low roughness of the carbon film allows the fuses to have a repeatable blowing voltage, with a thickness of 20 nm. Because the carbon is amorphous (Figure 3D), there are no grain boundaries that would cause resistivity variations between fuses, which would in turn cause a variation of the blowing voltage.

The high degrees of reproducibility of the $I$–$V$ measurement for 200, 150, and 100 nm indicate that slight process variations do not have a significant impact on device performance (Figure 4). At 60 nm, however, we see greater device-to-device variation in the $I$–$V$ curves, likely resulting from the larger impact of our lithography limitations and line-edge roughness on these smaller devices.

For the nanofuses to be used in data storage, the read and write voltages should work with standard computer drivers. This means that the write voltage should be below 3 V and the read voltage should be around 1 V. As the nanofuse width gets smaller, the voltage and current required to blow them also decrease (Figure 5). This trend allows for carbon nanofuses to have the blowing voltage tuned to above 1 V and below 3 V. To analyze any chemical bonding change in the carbon film due to annealing, we compared the normalized intensity ratio of the carbon k edge from the annealed and unannealed samples with sp² carbon standards (lacey carbon film and ultrathin carbon black, Ted Pella product #01824). These EELS results indicate that the thin-film carbon is composed of amorphous sp² carbon both before and after annealing. In short, despite the large change in resistivity due to annealing, no change in the structure, composition, or bonding of the thin-film carbon was observed.
The life expectancy (LE) of permanent data-storage media depends on the failure mechanisms present when data are being read, called read disturb (RD) errors, and when they are being stored, called data retention (DR) errors. Failure mechanisms in nanofuse-based data storage could include atomic diffusion, electromigration, oxidation, and other chemical changes. Key to having a long time scale for these degradation mechanisms is the fundamental stability of the chemical bonds of the materials that comprise the data-storage medium. The sp² carbon has a very high local bond strength, which should provide a significant stability advantage, leading to longer LEs. The chemical path most likely to result in the degradation of surface carbon is oxidation, but carbon does not readily oxidize below 300 °C and so would remain very stable at or near room temperature. In fact, we have seen no degradation in written or unwritten carbon nanofuses upon storage at room temperature over the several months this study was carried out.

Despite the high expected stability of carbon bonds in the bulk of these materials, we were particularly concerned about the stability of the surface carbon atoms and their stability under the RD conditions of data readout. Stability problems for metal fuses have been seen to primarily arise from the formation of dendrites in fuse gaps under applied electric fields (Figure 6E,F), resulting in current pathways when the fuse is broken, and data corruption. We therefore subjected carbon fuses to an accelerated testing of RD conditions and presented the results in Figure 6C,D. For both the intact and blown states of the nanofuse, the test voltage was applied for a time equivalent to the cumulative time that voltage would be applied during 10¹² reads without detecting any change in the nanofuses.

DR measurements on these fuses during storage are also important but will need to be carried out on far more devices than the few devices measured here. For such data to be relevant in the context of modern memory systems, this will require scale up (ultimately to gigabyte levels) of integrated devices so that relevant statistical analysis can be done and compared to that of other archival solid-state storage media.²⁶

**CONCLUSIONS**

Nanofuses for permanent data storage could be reliably produced with arc-deposited carbon. The arc-deposited carbon thin film shows predominantly sp² character and is electrically conductive and deposits uniformly. These carbon nanofuses are electrically stable for read voltages held over 90 h. Their writing time is under 200 ns, and they blow with power in the low milliwatt range. We also found the voltage and current requirements for fuses with lateral dimensions down to size smaller than in the previous graphene nanofuses. Both the power and voltage required to blow a carbon nanofuse decrease with fuse size, indicating that the writing voltage is tunable to fuse geometry. These studies provide data that will be valuable in determining the feasibility of manufacturing permanent memory from PVD-grown amorphous carbon and the productive fuse geometries.
AUTHOR INFORMATION

Corresponding Author
*E-mail: davis@byu.edu.

ORCID

Robert C. Davis: 0000-0002-6165-4396

Notes
The authors declare no competing financial interest.

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