Terabit-per-square-inch data storage with the atomic force microscope

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An areal density of 1.6 Tbits/in.^{2} has been achieved by anodically oxidizing titanium with the atomic force microscope (AFM). This density was made possible by (1) single-wall carbon nanotubes selectively grown on an AFM cantilever, (2) atomically flat titanium surfaces on α-Al_2O_3 (1012), and (3) atomic scale force and position control with the tapping-mode AFM. By combining these elements, 8 nm bits on 20 nm pitch are written at a rate of 5 kbit/s at room temperature in air. © *1999 American Institute of Physics.* [S0003-6951(99)02248-2]

The magnetic hard disk is the dominant method for storing data in the microelectronics industry. Its progress has been fueled by the ever-increasing demand for storage capacity coupled with the continual decrease in price per megabyte. In 1990, state-of-the-art hard disks had an areal density of less than 0.1 Gbit/in.^{2}; currently, disks with areal densities of 5 Gbits/in.^{2} are being sold. In the near future, it is expected that hard disk drive scaling, and the move to giant magnetoresistive heads, will push areal densities into the upper tens of Gbits/in.^{2}. This growth rate can be described by a 60% cumulative annual increase—at this rate, conventional scaling is expected to run out in 2006. This technological limitation will not stop the need for greater storage capacity in less space.

To displace magnetics as the mainstream method for data storage, an emerging technology must offer substantial advantage beyond the incremental advance of an existing technology. Many approaches have been brought forward; the two most prominent are nanoimprint and scanning probe. Chou and co-workers[1] have pioneered nanoimprintation as a method for fabricating 400 Gbit/in.^{2} read-only (compact disk) devices and 45 Gbit/in.^{2} read–write devices. Binnig *et al.*,[2] Mamin and Rugar,[3] and Chui *et al.*,[4] through a series of innovations, have pursued a read–write system based on scanning probes that has achieved an areal density of 400 Gbits/in.^{2}. Both of these techniques show clear paths to a complete data storage system.

We report here an alternative method for writing bits on a substrate. It is not the goal to show a complete system, but simply to locate what the authors believe to be the uppermost point for areal bit density obtained at room temperature and in air. There is a long history in the literature of surface modification with scanning probe microscopes,[5] however, none of these exceed the threshold of a terabit per square inch. Atomic and molecular scale modifications far surpass this threshold but are generally not suited for data storage because of their low-temperature or vacuum operation. Examples of this include Eigler and Stroscio using the cryogenic scanning tunneling microscope (STM) to move around single atoms,[6] and Gimzewski, Cuveres, and Schlittler using the vacuum STM to align C_{60} molecules on copper lattices.[7] Albrecht *et al.* have used the STM in air to ablate graphite to create sub-10-nm holes, however, this technique was often unstable as the ablation and imaging process can obscure adjacent patterns and damages tips.[8]

In this letter, we show that the tapping-mode atomic force microscope (AFM) can oxidize atomically flat titanium with a single-walled carbon nanotube to achieve a bit density of 1.6 Tbits/in.^{2} at a rate of 5 kbits/s. While this data rate is exceedingly slow for storage applications, parallelism, as demonstrated by the groups at IBM (Ref. 9) and Stanford,[10] can serve to overcome this limitation. Tapping mode is used to reduce lateral forces and permit operation with the single-walled nanotube (SWNT) tip. The nanotube tip allows for highly localized surface modification. Additionally, the extreme hardness and cylindrical shape of the nanotube alleviates bit degradation from tip wear during the write process, and minimizes tip convolution effects during the read process.

Bits were written in titanium using the electric field from the conductive nanotube to locally oxidize the titanium surface. Field-induced oxidation was originally developed on silicon with the STM by Dagata *et al.*[11] and on titanium with the STM by Sugimura *et al.*[12] Subsequently, Snow and Campbell developed field-induced oxidation of silicon with the AFM.[13] By this method, a scanning probe is brought in close proximity to a thin metal film and a negative bias voltage is applied to the probe tip in the presence of water adsorbed on the surface. This local oxidation has since been well characterized in terms of parameters such as tip diameter, substrate roughness, field strength, scanning rate, tip–sample distance, and environment.[14] However, the diameter

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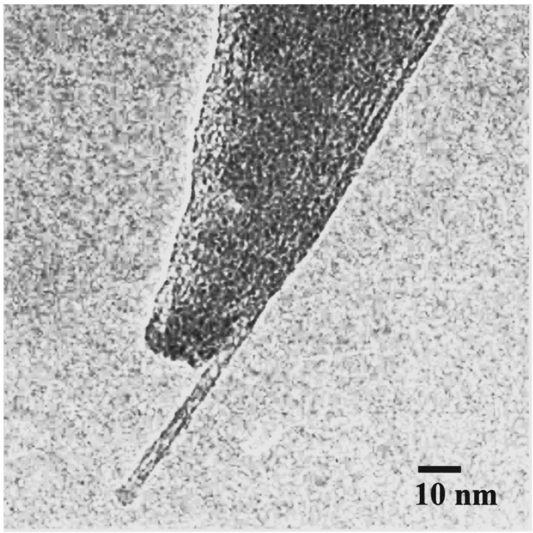

FIG. 1. Transmission electron microscope image of a single-wall carbon nanotube synthesized on the tip of a silicon AFM cantilever.

of the proximal probe tip and the surface roughness of the substrate ultimately limit the minimum attainable feature size.

In a recent demonstration using AFM lithography, multiwalled carbon nanotubes were used to write lines as narrow as 10 nm.[15] Nanotubes have proven to be quite resistant to wear, enabling them to write large areas without tip degradation. To obtain ultrahigh bit densities in this work, SWNTs, 2–5 nm in diameter, were used. The smaller diameter nanotube allows sub-10-nm features to be written, while at the same time permitting larger features to be written more reliably.

The single-walled carbon nanotube tips used here were synthesized by chemical-vapor deposition on the tip[16] of a commercial silicon cantilever (see Fig. 1).[17] First, a catalyst solution to promote SWNT growth was prepared by hydrolyzing $FeCl_3$ in ethanol to produce iron oxide. A supporting gel matrix was formed of aluminum and silicon oxides. Molybdenum oxide was used as a promoter. The tubes were dipped in the catalyst solution and then exposed to chemical-vapor deposition of CH_4 at 900 °C. Since the catalyst coats the entire surface of the cantilever tip, nanotubes grow at many sites and follow the contour of the surface. The sharp discontinuity at the pyramid tip allows the nanotube to extend beyond the surface, sometimes over a micron in length.

Tips synthesized by this process often have a single nanotube tip extending from the cantilever pyramid, although sometimes multiple nanotubes form small bundles. SWNT tips range in length from a few nanometers to more than a micron. After synthesis, most tips must be trimmed in order to isolate a single nanotube less than 65 nm long that is suitable for reliable imaging and writing. A tip that is too long will either buckle during writing, producing wider features, or traverse the surface with a slip–stick motion, producing intermittent oxidation.

Nanotube tips were shortened by applying a series of 500 μs voltage pulses ranging from 20 to 60 V between the nanotube and titanium surface. During the tip-shortening process, a commercial AFM (Ref. 18) is used to measure the root-mean-square (rms) amplitude and deflection of the cantilever versus tip–sample separation. The cantilever is driven at resonance while a piezotube scans the cantilever over a range of a few hundred nanometers in a direction orthogonal to the substrate. The scan range of the tip–sample separation is adjusted so that the tip only contacts the surface for the last ~10 nm of the scan. A noticeable shift in the amplitude and deflection curves occurs when the tip is successfully shortened. Figure 2 shows the response from a nanotube which has been shortened to ~45 nm.

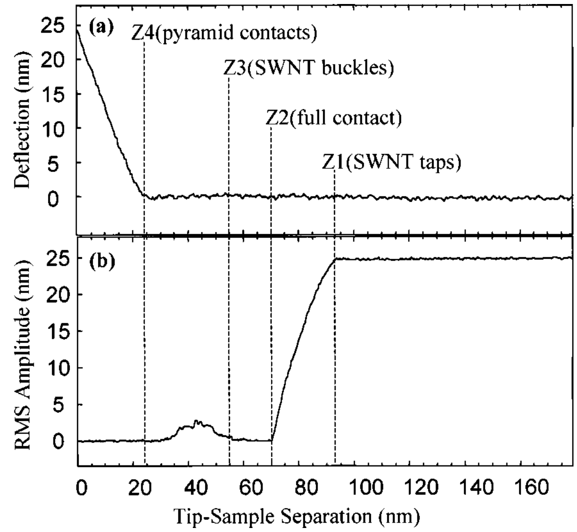

FIG. 2. (a) Tip deflection and (b) rms amplitude of a mechanically driven cantilever as a function of tip–sample separation. When the tip is far from the surface, the cantilever oscillates freely. As the tip is brought in contact with the surface (Z1), the oscillation amplitude is reduced, until the tip is in full contact with the surface (Z2), at which point the rms amplitude is zero. The tip is lowered another 15 nm further towards the surface until it buckles (Z3). The length of the nanotube is shown between the point where the nanotube is first in contact (Z2) and where the pyramid contacts the surface and the cantilever deflects linearly (Z4).

Our substrate consists of a 2-nm-thick conformal layer of titanium on an atomically flat α-Al_2O_3 (1012) surface.[19] The surface roughness is approximately 1 Å, which is critical for two reasons. First, it allows consistent, repeatable lithog-

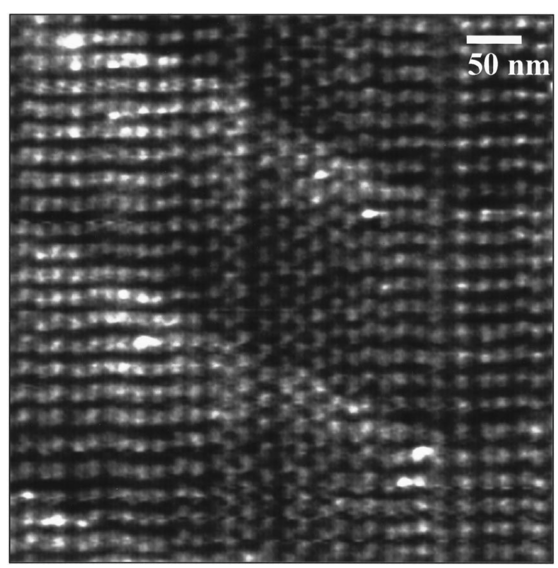

FIG. 3. 500 nm×500 nm tapping-mode AFM image of a high-density bit array taken from a 16 μm^2 patterned area. The vertical scale is 2 nm. The crystal planes of the substrate can clearly be seen.

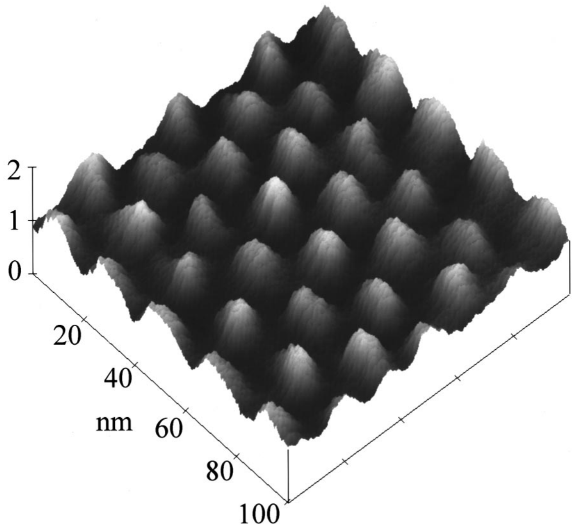

FIG. 4. 100 nm×100 nm×2 nm surface plot of ~8 nm bits with a ~1 nm titanium oxide height.

raphy. Extreme discontinuities in the surface cause sticking and deformation of patterned features. Second, since the average height of the titanium oxide bits is approximately 1 nm, high surface roughness can cause ambiguity in reading features.

Bits were both patterned and imaged in the tapping mode.[16] For writing, a 5 kHz square wave of $+0.5$ and -9.5 V was applied to the tip. Low voltages will not induce oxidation, and very high voltages will produce excessively large features.[14,20] An average tip velocity of 100 μm/s was used to produce 8 nm bits at a 20 nm pitch, which is equivalent to a bit density of 1.6 Tbits/in.^{2}. The images in Figs. 3 and 4 were taken from a 16 μm^2 area that had been completely patterned with bits. Several such areas were written with a single nanotube tip, without degradation of resolution or uniformity. Bits as small as 6 nm in diameter were written at 12–15 nm spacing by adjusting the frequency of the control voltage, and the tip velocity. SWNTs allow significantly faster writing rates compared to conventional silicon cantilever tips, which typically write at rates equivalent to 5–30 bits/s when producing oxide of comparable height.[14]

We extend improvements to feature sizes achievable with AFM field-induced oxidation by combining single-walled nanotube tips with an atomically flat substrate. This allowed us to demonstrate controllable data storage at densities upwards of 1.6 Tbit/in.^{2}. The success of this lithography is highly dependent on the length, stiffness, and diameter of the SWNT tip. The lithography approach described here is not limited to data storage applications, but can be extended to other sub-10-nm nanofabrication applications.

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