Carbon-Coated Tellurium for Optical Data Storage

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ABSTRACT A highly durable optical disk has been developed for data archiving. This optical disk uses tellurium as the write layer and carbon as a dielectric and oxidation prevention layer. The sandwich style CTeC film was deposited on polycarbonate and silicon substrates by plasma sputtering. These films were then characterized with AFM, SEM, TEM, EELS, and ellipsometry and were tested for writability and longevity. Results show the films were uniform in physical structure, stable, and able to form permanent pits. Data was written to a disk and successfully read back in a commercial DVD drive.

KEYWORDS: data storage • archival • tellurium • optical disk • DVD • carbon

INTRODUCTION

In the past decade, significant progress has been made in data storage technology, both in capacity and speed. High-capacity hard drives, flash memory, and Blu-ray optical disks are current examples of the continuing trend toward higher capacities and faster seek times. One area that seems to have been neglected in all of these developments is the long-term storage of digital data; by long-term, we mean storage for hundreds of years. Magnetic hard drives, flash memory, and current optical disk technologies are not appropriate for long-term data storage because of their short data storage lifetimes (1−3). Currently, to the best of our knowledge, nearly all write once read many (WORM) DVD media are dye-based, even so-called archival grade media. Studies show that the lifetime of those media fall short of the 100+ year goal (4−6).

Tellurium-based optical disks were explored in the early 1980s. Terao et.al. found that tellurium and some of its alloys made cleaner pits under exposure to a write laser than the other materials investigated (7). Lou et al. made a disk with a tellurium write layer and investigated the recording stability, data density, error statistics and archival stability of their disk structure (8). Kivits et al. and Suh et al. have studied the mechanisms for hole formation in a thin tellurium film (9, 10). Herd investigated tellurium with a top layer of carbon (11). However, concerns with oxidation of the tellurium layer and the development of tellurium alloys for rewritable DVD applications seem to have led to a decline in the development of tellurium as a write once, read many (WORM) write layer.

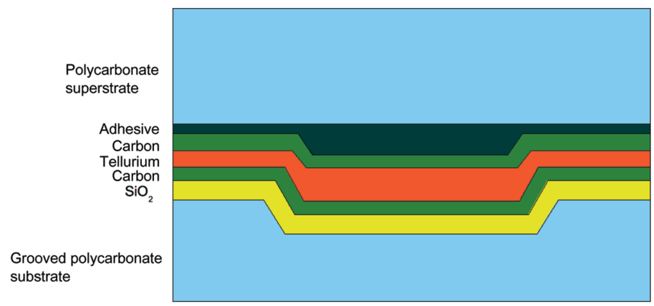

FIGURE 1. Schematic representing the structure of the CTeC disk.

In this paper we present an archival optical disk using a novel carbon−tellurium−carbon (CTeC) sandwich as the write layer, see Figure 1 for a diagram. The carbon thin films were employed to protect the tellurium layer from oxidation-induced degradation. The CTeC sandwich write layer was prepared using plasma sputtering deposition and characterized with AFM, TEM, and spectroscopic ellipsometry. The written marks were imaged by AFM, TEM, SEM, and optical microscopy, and a Pulstec ODU 1000 was used for writing and analysis of digital errors. Writing and stability tests show that permanent pits can be written to CTeC-based disks, and that the disks are resistant to degradation and subsequent data loss. The disk currently being manufactured and sold by Millenniata, Inc. (Provo, UT), which meets industry specifications, is similar in many ways to the disk presented in this paper, including its use of carbon layers.

EXPERIMENTAL MATERIALS AND METHODS

The thin films used in this study were deposited in a PVD 75 system (Kurt J. Lesker, Clariton, PA) by magnetron sputtering. The base pressure was 10^{-5} Torr before deposition and the pressure rose to 1×10^{-3} Torr during deposition. Carbon was

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reactively sputtered from a 99.999% graphite target at a power of 400 W. Tellurium was reactively sputtered from a 99.999% elemental target at a power of 20 W. Silicon dioxide was reactively sputtered from a 99.9999% elemental silicon target using 99.999% oxygen in argon. The carbon layers were 13−20 nm thick, the tellurium layers 20−30 nm, and the silicon dioxide layer was 20−70 nm thick.

Film thicknesses were controlled by deposition time, which were informed by AFM step height measurements. To get accurate step height measurements, a marking pen lift-off technique was used to create the step edge in the deposited films. A line was drawn with a Sharpie fine-tipped permanent marker on a clean piece of silicon before depositing a film for a known time. After deposition, the silicon substrate was rinsed in acetone to remove the line from the permanent marker, and then rinsed in isopropyl alcohol and deionized water. This process left a clean edge suitable for measuring film thickness. AFM was also used to obtain film roughness data, and film thickness was used in conjunction with spectroscopic ellipsometry to determine optical constants of deposited films.

Films were typically deposited onto grooved polycarbonate substrates, 600 μm thick, although some films were deposited onto silicon substrates. Prior to deposition, silicon substrates were cleaned with soap and water, rinsed in deionized water, then dried with a jet of dry nitrogen. They were subsequently placed in an air plasma for 5 min. The polycarbonate was used as received from the manufacturer.

After deposition, the polycarbonate substrates were bonded to an ungrooved polycarbonate superstrate with a UV cure adhesive before writing with the ODU system. Writing was done with a Pulstec ODU 1000 system (Pulstec, Hamamatsu, Japan). This system was used to develop the write strategy (tuning the laser pulse durations and powers), write data to the disks, and perform digital error analysis.

After writing, the polycarbonate superstrate was removed and the exposed, written films were imaged with SEM and AFM. AFM data were collected on a Dimension V (Veeco, Camarillo, CA) in tapping mode. SEM images were acquired in a Phillips XL S-FEG (FEI, Hillsboro, OR).

To prepare a film for viewing in the TEM, we cut a small piece out of the substrate, and the film on this small piece was lightly scratched with a scalpel into squares approximately 5 mm on a side. The piece was then placed in dichloroethane. When the film released from the substrate, it was lifted out of the solvent with a 200 mesh copper TEM grid and was then ready for viewing. The carbon film used for EELS (electron energy loss spectroscopy) was deposited onto a silicon substrate using the same process conditions as the disks and the sample was then thinned by tripod polishing.

Cross sections for viewing in the TEM were created in a Helios NanoLab 600 DualBeam (FEI) system. A small piece was cut from the film-coated substrate and mounted on a sample stub. The sample was coated with a thin (5−10 nm) layer of gold to reduce charging of the polycarbonate substrate. 50 nm of platinum was deposited in situ with the electron beam to limit damage to the sample surface, after which 1 μm of platinum was deposited with the ion beam. A TEM sample was cut, lifted out, attached to a half copper washer, and thinned for TEM viewing in the DualBeam chamber. The sample was then ready for TEM examination in a Tecnai F20 analytical STEM (FEI).

RESULTS

We first present characterization of the physical structure of the layers represented in Figure 1. Figure 2A shows a cross-section viewed in the TEM in STEM mode; the contrast has been adjusted to make some layers more visible in the right half of the image. The top layer is platinum deposited in the FIB as a protective layer. The bright layer below is the

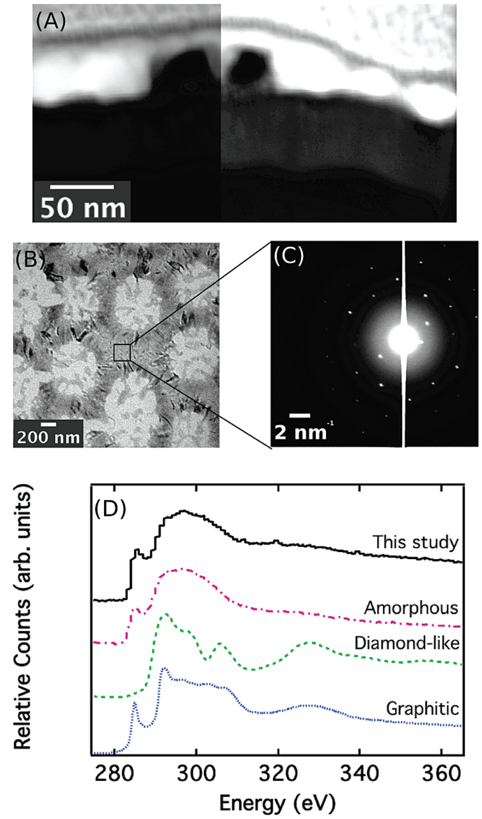

FIGURE 2. Characterization of the write layer materials. (A) STEM cross section of the write layer. It is unclear whether this image is from a written or unwritten area of the disk. (B, C) Bright-field TEM plan view of the write layer and a SAD pattern taken from the area highlighted by the box. (D) EELS spectrum from the carbon layer with comparison spectra.

tellurium, and the dark lines visible on either side of the tellurium are the carbon layers. Under the bottom carbon layer, the silicon dioxide layer is visible, beneath which is the polycarbonate substrate. In the as-deposited state (prior to writing), EDX line scans of the cross-section confirmed that there was limited interdiffusion of the tellurium into adjacent layers as indicated by relatively distinct boundaries between layers.

We also investigated the crystallinity of the deposited layers. Figure 2B shows a TEM bright field image of written pits, which are the brighter oval areas. A diffraction pattern was taken from a small area between the written marks, as indicated by the black box. The diffraction pattern is shown in Figure 2C, and appears to come from a single-crystalline grain of tellurium. The aperture diameter in the imaging plane was measured at 190 nm. The tellurium layer is polycrystalline with an approximate grain size of at least 200 nm.

The internal bonding of the carbon layers was investigated by EELS, with the result shown in Figure 2D. Three reference spectra, graphitic, diamond-like, and amorphous carbon, are shown for comparison. Although the intensities or heights of the peaks may vary somewhat, the general shape of the curve and/or peak ratios should not change significantly between similar materials. The spectrum obtained from our film has a small sharp peak at 285 eV, followed by a broad peak centered at about 296 eV. This

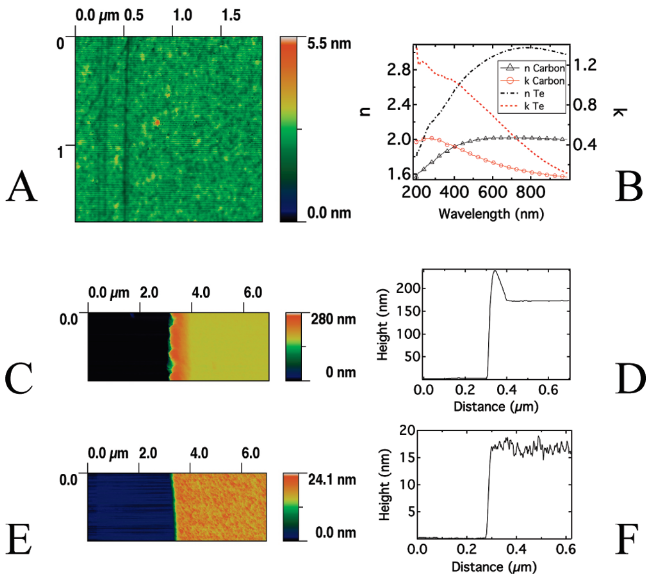

FIGURE 3. AFM and spectroscopic ellipsometry analysis of the write layer. (A) Tapping mode AFM image of a silicon shard. The surface roughness was 1.4 ± 0.5 Å. (B) Spectroscopic ellipsometry measurements of individual carbon and tellurium films. (C, D) Tapping mode AFM image of a tellurium film step edge and profile. The roughness of the tellurium film was 7.9 ± 0.3 Å. (E, F) Tapping mode AFM image of a carbon film step edge and profile. The roughness of the carbon film was 5.2 ± 0.1 Å.

matches well with the shape of the amorphous carbon spectrum, while the graphitic and diamond-like spectra both have features that are not seen in the spectrum of our material. From this, we conclude that the carbon layer in our films is amorphous.

Results of the AFM measurements and ellipsometry are shown in Figure 3. Figure 3A shows a tapping mode AFM image of a bare silicon shard, which is similar to the silicon substrates used to obtain the results in panels C and D in Figure 3. In Figure 3B, the optical constants for the individual carbon and tellurium films are plotted versus wavelength. In Figure 3C−F we investigated film roughness and used the step heights to determine deposition rates. Images C and E in Figure 3 show the z-sensor image of the step edge for the tellurium and carbon films, respectively. Profiles were extracted and are shown panels D and F in Figure 3 for the tellurium and carbon films, respectively.

In addition to investigating the layers themselves, written marks were examined. The optical contrast can be seen in the high frequency (HF) trace shown in Figure 4A, which shows the voltage on a photodiode while reading a disk in the ODU 1000 before removing the superstrate. The contrast can also be seen in Figure 4B, which is a reflected light optical micrograph taken after the superstrate was removed.

SEM and AFM were used to investigate the dimensions of the written marks. Figure 4C shows a SEM image taken at normal incidence with a beam energy of 5 keV, using the TLD detector. The dark areas are the written pits, the bright flecks inside the pits are particles of tellurium that remain after the writing process. Figure 4D is a 10 × 10 μm^2 AFM image, collected in tapping mode, of the written pits. A profile was extracted from the line down the middle of the

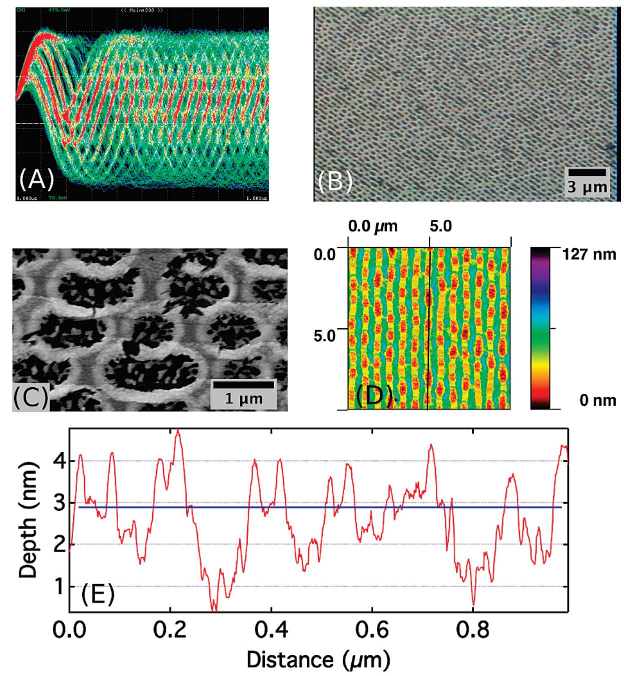

FIGURE 4. Analysis of the written pits. (A) HF trace showing the contrast between reflective lands and nonreflective pits for all the different sizes of pits superimposed. (B) Optical micrograph of the written pits. (C) SEM image of written pits. The bright rings around the pits are caused by an accumulation of material around them when the pits are written. (D) Tapping mode AFM image of written pits. (E) Profile taken along the line shown in D. The writing process forms pits in the write layer.

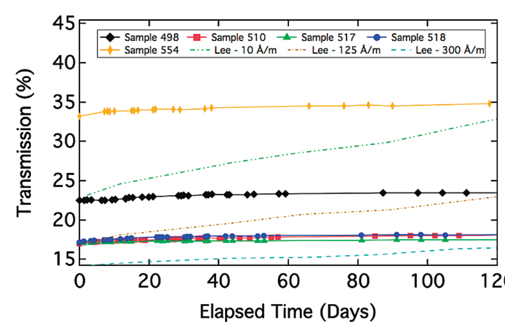

FIGURE 5. Optical transmission of five different write layers (shown in the solid lines) were measured over 120 days at room temperature. Optical transmission of bare tellurium films from Lee and Geiss is shown in the dashed lines for comparison.

figure along one of the data tracks and is shown in Figure 4E. The horizontal line in Figure 4E was determined by examining the unwritten areas between marks and indicates where the level of the unwritten film is.

To test the stability of the CTeC films, optical transmission was measured over 120 days. During that time the disks were kept in ambient lab conditions (22 °C, and the humidity varied between 5 and 50% Rh depending on the weather). The solid lines in Figure 5 are from CTeC films, the dashed lines are from comparison tellurium films, without a carbon layer, from Lee and Geiss (12).

Data-to-clock jitter is a measure of the definition of pits and lands on a disk (2). If the transition from pit to land or vice versa is not clean (sloped pit edge, jagged border, incorrectly formed pit, etc.) it will result in a higher jitter value. The DVD specification states that the jitter cannot be

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Table 1. Average Values from 4 Disks That Were Read in an Off-the-Shelf Commercial Drive; Reflectivity Was Measured at 650 nm

parameter	value
write power (mW)	15.4 ± 0.5
data-to-clock jitter (ns)	4.99 ± 0.30
reflectivity before write (%)	25.4 ± 0.59

greater than 9% of a clock cycle; with a clock cycle of 38.32 ns, data-to-clock jitter should not exceed 3.44 ns (13). Table 1 lists average values for the data-to-clock jitter as well as average write power and reflectivity before the write.

DISCUSSION

Although our disk misses the DVD specification, it is significant that it can be read back in commercial drives and exhibits exceptional stability. Further optimization should yield, and indeed has yielded, a film that ultimately meets the required industrial specification. As seen in the optical micrograph in Figure 4B, the pits generally appear to be well-defined. In the SEM and TEM images, there were tellurium nanoparticles that did not move during the write process, but those nanoparticles did not appear to affect the optical contrast or our ability to read the data from the disks. From Figure 4E, we can see that the accumulation rings visible in the SEM and TEM are less than 5 nm tall and a few tens of nanometers wide. These accumulation rings have been seen before in the literature (see references already given). It is possible, but by no means proven, that the rings of material contribute negatively to the jitter value; however, as noted, we were still able to read the data from the disks in off-the-shelf commercial drives. The carbon layers do not negatively impact our ability to make pits in the tellurium.

The CTeC stack shows promise as a long-term data storage layer. The optical transmission of the CTeC layer did not change appreciably after the 15 day point, while plain tellurium films showed 12 to 30% increases in transmission that continued after 120 days. These effects were attributed to tellurium oxidation. Lee and Geiss saw a dependence of oxidation rate on the rate of film deposition, with slower oxidation rates occurring with faster film depositions (12). The CTeC films used in this study were deposited relatively slowly, 2−8 nm/min, so their relatively low oxidation rate cannot be attributed to fast deposition rates. Also, in previous work, it was observed that the tellurium layer would oxidize locally at defects (rougher areas, scratches, etc.) in the substrate (14). The carbon film onto which the tellurium layer was deposited was seen to be very smooth, thus reducing the likelihood of oxidation of the tellurium layer.

CONCLUSIONS

We have made a recordable disk with a novel write layer consisting of layers of carbon and tellurium. The data on the recorded disks were readable in off-the-shelf drives. We have characterized the composition and structure of the layers and found that they represent a system with potential for long-term stability. This system shows promise as an archival data storage material.

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