Nitrogen plasma treatment for continuous ultra-thin carbon nitride film on magnetic hard disk

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1. Introduction

Carbon nitride is the protective overcoat material of choice for magnetic hard disk in hard disk drives (HDDs). It provides good durability from the quasi-contact head-interface condition in hard disk drive. Current carbon nitride thin film used in the state of art hard disk drive stands at approximately 2 nm in thickness. Magnetic hard disk diameter ranges from 65 mm to 95 mm.

Maintaining protective thin film continuity so it is able to function effectively as a barrier to moisture and bonding sites for lubricant is increasingly difficult due to reduction in carbon thin film thickness for areal density gain [1]. Higher areal density per magnetic disk translates to lower cost for HDDs. The columnar structures of the cobalt chromium magnetic layers makes coverage by overcoat carbon nitride thin film more difficult. Figure 1 is the cross section TEM image of a typical magnetic hard disk. Thin film continuity becomes worse as thickness is reduced. Galvanic corrosion will occur more readily due to moisture percolation through weak/thinner spots on the magnetic hard disk carbon nitride thin film. This leads to cobalt dissolution from water that has percolated through. Data stored in the cobalt chromium magnetic grains become unreadable when corrosion occurs.

Carbon nitride thin films used in magnetic hard disk were deposited with heated filament plasma enhanced chemical vapor deposition (heated PECVD). This deposition method is widely use partly due to its simplicity and capability to deposit uniformly on a large surface. The mixing of plasmarized nitrogen gas with plasmarized hydrocarbon gas prior to deposition is the most commonly deployed method to obtain carbon nitride thin films in magnetic hard disk. Nitrogenated sites are spread throughout the carbon thin film [2]. Probability of moisture percolating through the carbon thin film is thus higher. The thin film continuity can be improved if deposition of carbon and nitrogen ions were separated. After the carbon thin film is deposit, practitioner can then nitrogenized its surface with low energetics plasmarized nitrogen. Nitrogenated sites were restricted to the top most surface of the thin film [3]. Figure 2a is the schematic diagram of carbon nitride thin film deposited by mixing hydrocarbon gas with nitrogen gas. Figure 2b is the schematic diagram of carbon nitride thin film deposited via post nitrogen plasma treatment. The nitrogenized sites were restricted to the top most surface.

The corrosion resistance of the ultra-thin carbon films with different amount of nitrogen content was characterized via cobalt extraction method. The roughness of the magnetic media was measured with an AFM. The penetration depths of the nitrogen ions were determined with Auger Electron Spectroscopy (AES). The carbon thin film affinity for functional perfluoropolyether (PFPE) lubricant with different amount of nitrogen was compared as well.

2. Experiment

Magnetically good production 65mm circular glass substrate disks were used. Experiments were conducted in a class 100 clean room at 25°C. Six different nitrogen content magnetic hard disk were prepared. Thin films deposition and nitrogen plasma treatment processes were done sequentially without breaking vacuum. Table 1 is the experimental matrix.

<table>
<thead>
<tr>
<th>Carbon Nitride</th>
<th>Magnetic layers</th>
</tr>
</thead>
</table>

(a) Carbon Nitride CoCr based magnetic layers

(b) Figure 2 Schematic diagram of carbon nitride film deposited on magnetic layers of a hard disk by (a) Mixing hydrocarbon and nitrogen gas (b) Post nitrogen plasma treatment

Table 1 Experimental matrix
2.1. Cobalt extraction test

Cobalt decoration on the surface of the magnetic disk signals the start of galvanic corrosion [4]. Susceptibility of the magnetic hard disk to corrosion can be determined by the amount of cobalt detected on the surface.

One nanometer of functional PFPE lubricant known as D4OH was first coated onto the magnetic hard disk carbon nitride film via standard dip and coat method. The bonded ratios of the lubricant thin films were then set to 80% via deep UV irradiation at 185nm.

0.5ml of 3% concentrated nitric acid was titrated onto four spots of the UV irradiated magnetic hard disk. The titrated spots have a diameter of 9mm. The titrated magnetic hard disk were left in a clean bench for approximately 60 minutes before being extracted using a pipette. The extracted acid was then analyzed by inductively coupled plasma mass spectrometry (ICP-MS) for cobalt. The model of the ICP-MS is Perkin Elmer Elan. Two surfaces were measured for each experimental cell.

2.2. AFM

The roughness of the carbon thin film on magnetic hard disk was measured with a DI 3100 (nanoscope V) AFM. Scan areas were 1µm by 1µm. Scan line was 256 with 256 sample per line at 1hz frequency. Bruker TESP-V silicon etch tip with nominal radius of 7nm was used in tapping mode.

2.3. Lubricant affinity test

Magnetic hard disk of different nitrogen amount were dipped consecutively into the fluorinated solvent known as Vertrel containing 40ppm of functional PFPE lubricant known as D4OH and pulled up at a controlled speed of 1mm/s. The lubricant film thickness was then measured by Fourier Transformed Infra-Red (FTIR) accessorized with a grazing angle accessory. The absorbance intensity at 1285cm⁻¹ was used to determine the lubricant thickness which was previously correlated with Electron Spectroscopy (ESCA).

2.4. Nitrogen depth profile

The Auger Electron Spectroscopy (AES) made by JEOL Ltd (Model: JAMP7800F) was used to detect C, N, O and Co elements on surface of the carbon thin film. Auger primary electrons energy was set to 10keV. The sample was bombarded with Ar⁺ at 1keV and analyze with AES to obtain elemental depth profile. The bombarded area was about 2nm by 2nm. Each bombardment cycle was 10s. This was repeated 10 times. The removal rate was estimated to be 0.0101nm per cycle. This was based on previous correlation sample.

3. Results and discussion

Corrosion resistance of the magnetic hard disk becomes worse with higher amount of nitrogen content. The average amount of cobalt extracted per centimeter square increase exponentially when the nitrogen content is larger than 6%. The average cobalt level on the magnetic hard disk for cell 1 to cell 6 were 0.028ng/cm², 0.0235ng/cm², 0.037ng/cm², 0.0475ng/cm², 0.1045ng/cm² and 0.3 ng/cm² respectively. Refer to Figure 3.

![Figure 3](image3.png)

Figure 3 Average Cobalt level (ng/cm²) extracted from magnetic hard disk surfaces versus Nitrogen Content (%) in carbon thin films via cobalt extraction test

Roughness of the carbon thin film on magnetic hard disk was measured. Average roughness (Ra) ranges from 0.23nm to 0.32nm and root mean square roughness (Rq) ranges from 0.29nm to 0.32nm. Refer to Figure 4. There is no correlation between nitrogen content and roughness. Maximum differences is less than 0.1nm for Ra and 0.03nm for Rq. Post sputter plasma treatment have no significant effect to carbon thin film roughness.

![Figure 4](image4.png)

Figure 4 Roughness (nm) of carbon thin film on magnetic hard disk versus experiment cell (#)

The nitrogen plasma treated magnetic hard disk lubricant affinity increase linearly as the nitrogen content increases. Lubricant thickness of cell 1 to 6 was 1.25Å, 6.11Å, 8.38Å, 9Å, 10.07Å and 10.53Å respectively. Refer to Figure 5. This is similar to carbon thin film

![Figure 5](image5.png)
deposited by mixing precursor gas with nitrogen during deposition [5]. Higher lubricant affinity was deemed more desirable. Lubricant film conformations on magnetic hard disk are flatter when the lubricant affinity is high. This translates to better flyability for the magnetic head flying at close proximity during operation [6]. Flyability is an important enabler for higher areal density in hard disk drive.

![Figure 5](image)

**Figure 5** Lubricant thicknesses (Å) on carbon thin film versus Nitrogen content (%) in carbon thin film via lubricant affinity test

Nitrogen ions percolations in magnetic hard disk carbon thin film were envisioned to be higher with higher nitrogen content. This was confirmed through nitrogen depth profiling of carbon thin film.

Refer to Figure 6. The nitrogen ions content from 0 to 1nm for cell 2 to 6 were plotted. The amount of nitrogen found on the top (0 nm) were highest for cell 6 follow by cell 5, cell 4, cell 3 and cell 2. An exponential decrease in nitrogen ions as the depth increases. Experiment cells with higher amount of nitrogen ions will continue to have higher amount than those with lower initial amount deeper into the carbon thin film. For example, cell 6 (N2=15.5%) nitrogen ions remains detectable until 0.8nm while cell 2 (N2=6%) nitrogen ions becomes non detectable at 0.2nm.

![Figure 6](image)

**Figure 6** Nitrogen concentrations in magnetic hard disk carbon thin film versus depth (nm)

### 3.1. Nanocracks

Hard disk lubricant adhere to the carbon thin film via hydrogen bonding and bona fide chemical bonding [7]. Based on the lubricant affinity test, we know carbon nitride thin film have a higher polarity/affinity for lubricant compared to hydrogenated carbon thin film (Cell 1). The affinity increases with increasing amount of nitrogen content. Hydrogen bonded lubricant on the carbon thin film maybe remove by rinsing with a suitable fluorinated solvent. We used fluorinated solvent marketed by Dupont known as Vertrel-XF to rinse the lubed magnetic disk [8]. The residual lubricant retains on the carbon thin film after rinsing should consist mainly of bona fide chemical bonded lubricant. Bona fide chemical bonding process as stated by Kasai refers to “entailed migration of OH-bearing end group into intra-granular crevices of carbon overcoat” [7].

Magnetic hard disks were lubed to a thickness of 9Å ± 1Å via the stand dip and pull method before rinsing in pure Vertrel-XF. Refer to Table 2. The bonded lubricant ratio increases from 11.7% when nitrogen content is zero till 55.5% when the nitrogen content is at 15.5%. There are more intra-granular crevices on the magnetic hard disk with higher nitrogen content.

![Table 2](image)

**Table 2** Bonded Ratio of after lubricated magnetic disk

<table>
<thead>
<tr>
<th>Cell</th>
<th>Nitrogen Content (%)</th>
<th>Bonded Ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>11.7 ± 2.9</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>37.2 ± 2.5</td>
</tr>
<tr>
<td>3</td>
<td>8.5</td>
<td>42.2 ± 1.2</td>
</tr>
<tr>
<td>4</td>
<td>11</td>
<td>45.0 ± 2.4</td>
</tr>
<tr>
<td>5</td>
<td>14</td>
<td>53.2 ± 3.8</td>
</tr>
<tr>
<td>6</td>
<td>15.5</td>
<td>55.5 ± 6.4</td>
</tr>
</tbody>
</table>

Fractures or cracks on thin films were due to film stress. Carbon thin film cracks and stress on magnetic hard disk was envisaged as being higher with larger amount of nitrogen content. If this holds true, higher nitrogen content on carbon thin film should translate to higher corrosion. The probability of moisture ions percolating through the carbon thin film becomes higher due to shorter “travel distance” and larger amount of nanocracks. This was confirmed through to our experiment. Refer to Figure 3 for the corrosion resistance result and Figure 6 for the nitrogen penetration depth. Figure 7 is the schematic diagram of the carbon thin film with nanocracks.

![Figure 7](image)

**Figure 7** Schematic diagram of carbon thin film with (a) longer cracks that are close to the magnetic layers (b) shorter cracks further away from magnetic layers

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**Figures and Tables**: These figures and tables are placeholders. Actual figures and tables should be included in the document for a complete understanding of the content.
An optical scan analyzer (OSA) was used to scan the topology of the carbon thin film. It is capable of measuring surface topography to angstrom level sensitivity [9]. Figure 8 is a typical image of the magnetic hard disk used for this experiment. The different shades represent the thickness of the carbon thin film. Darker regions infer higher carbon thickness. The max carbon thickness difference between darkest and lightest region is approximately 3Å. We did not detect any visible cracks or abnormalities on the magnetic hard disk used for this experiment.

**Figure 8** OSA of a typical magnetic hard disk after nitrogen plasma treatment

4. Conclusion

Continuity of the ultra-thin carbon nitride film (<2nm) maybe controlled via low energetics plasma nitrogen species. The ultra-thin carbon nitride film roughness changes were less than 0.1nm. It displays similar lubricant affinity as those deposited by mixing precursor gas. This technique will be useful to practitioner when ultra-thin film continuity is of prime importance. It is also useful when one needs to precisely controlled corrosion resistance of a material with an ultra-thin protective overcoat.

The corrosion behavior and lubricant affinity of nitrogen plasma treated magnetic hard disk may be explained by the amount of nanocracks in the carbon nitride thin film.

5. References


