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Reuben Jueyuan Yeo

Ultrathin Carbon-Based Overcoats for Extremely High Density Magnetic Recording

Doctoral Thesis accepted by
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Supervisor's Foreword

Carbon is a highly versatile element that is capable of forming a variety of allotropes that exhibit a diverse range of physical properties, which is primarily attributed to the way carbon is bonded in a material. Diamond, one of the well-known carbon allotropes, is the hardest material known to man because of its strong sp^3 hybridized covalent bonding in a rigid tetrahedral crystalline structure. In contrast, graphite, which comprises only sp^2 hybridized covalent bonding, shears easily and is widely used as a solid lubricant. Between these two extremes, amorphous carbon is another allotrope of carbon that contains a mixture of both sp^2 and sp^3 hybridized bonds within a disordered matrix.

Amorphous carbon thin films have attracted significant interest to be applied as protective overcoats in magnetic storage systems. This is because not only do they exhibit chemical stability, mechanical toughness and high smoothness, they can easily be fabricated at room temperatures using conventional plasma-based processes. For hard disk drives (HDDs), amorphous carbon thin films are used as overcoats on both the recording disk media and head. While the media overcoat protects the soft magnetic media from wear and corrosion, a monolayer of perfluoropolyether (PFPE) lubricant that is applied on top of the media overcoat lowers the friction for higher wear life. At the same time, the head overcoat protects the magnetic elements in the head from wear and corrosion, and additionally acts as a form of tribo-chemical protection to isolate the PFPE lubricant from the head substrate. Nevertheless, the ever-growing demand for extremely high density data storage necessitates the reduction of the amorphous carbon overcoat thickness to an order of less than two nanometers, which would eventually lead to deterioration of the overcoat's protective qualities. Furthermore, with the HDD industry gearing towards heat-assisted magnetic recording (HAMR), the overcoat has to be thermally stable against temperatures of up to 500 °C. At this ultrathin regime, the sp^3 bonding, which is responsible for the overcoat's desirable structural and mechanical properties as well as its thermal stability, is drastically reduced. On the other hand, tape drive heads are constantly subjected to aggressive wear by the tape, hence maintaining high wear durability of the tape head overcoat is most crucial.

In his doctoral thesis, Reuben Yeo employs two approaches simultaneously to improve the protective characteristics of amorphous carbon overcoats at the ultra-thin level. Firstly, the introduction of an atomically-thick interlayer of silicon nitride (SiN_x) served to improve the adhesion between the substrate and the carbon overcoat through the formation of extensive interfacial bonding, and at the same time acted as a barrier layer between the overcoat and the substrate to reduce the catalytic sp^3 to sp^2 bonding transformation. Secondly, the energetic filtered cathodic vacuum arc (FCVA) process was used to enhance the sp^3 bonding as well as to create atomic intermixing at the interface for better adhesion. As described in the thesis via appropriate characterization techniques, both approaches worked synergistically to obtain an ultrathin carbon-based overcoat with superior corrosion protection, wear durability and thermal stability. In the final part of the thesis, Reuben Yeo challenges the reader to push the thickness boundary to its limits, by exploring graphene as a possible novel two-dimensional overcoat material for HDD recording media.

With the dawn of the age of nanoscience and nanotechnology, Reuben Yeo's thesis could not have come at a more opportune time due to its technological relevance and scientific impact. His thesis provides insightful discussions on how, at the nanoscale, tailoring the microstructure as well as the surface and interface chemistry can affect the tribological and corrosion properties of ultrathin carbon films. Even though this thesis focuses mainly on magnetic storage systems applications, the methods and strategies employed in tailoring the properties of ultrathin carbon-based overcoats can also be applied to other nano-coating materials, as well as for applications as diverse as MEMS/NEMS, biomedical devices, cutting tools, and pipeline coatings.

Singapore
October 2016

Prof. Charanjit Singh Bhatia

Parts of this book have been published in the following journal articles:

In Chapter 4:

1. **R. J. Yeo**, E. Rismani, N. Dwivedi, D. J. Blackwood, H. R. Tan, Z. Zhang, S. Tripathy, and C. S. Bhatia, "Bi-level surface modification of hard disk media by carbon using filtered cathodic vacuum arc: reduced overcoat thickness without reduced corrosion performance", *Diamond and Related Materials* **44**, 100 (2014). Reprinted with permission from Elsevier. Copyright (2014).
2. N. Dwivedi, N. Satyanarayana, **R. J. Yeo**, H. Xu, K. P. Loh, S. Tripathy, and C. S. Bhatia, "Ultrathin carbon with interspersed graphene/fullerene-like nanostructures: a durable protective overcoat for high density magnetic storage", *Scientific Reports* **5**, 11607 (2015). Reprinted under the Creative Commons CC-BY 4.0 license.
3. S. Kundu, N. Dwivedi, N. Satyanarayana, **R. J. Yeo**, J. Ahner, P. M. Jones, and C. S. Bhatia, "Probing the role of carbon microstructure on the thermal stability and performance of ultrathin (< 2 nm) overcoats on $L1_0$ FePt media for heat-assisted magnetic recording", *ACS Applied Materials & Interfaces* **7**, 158 (2015). Reprinted with permission. Copyright (2014) American Chemical Society.
4. P. S. Goohpattader, N. Dwivedi, E. Rismani-Yazdi, N. Satyanarayana, **R. J. Yeo**, S. Kundu, and C. S. Bhatia, "Probing the role of C^+ ion energy, thickness and graded structure on the functional and microstructural characteristics of ultrathin carbon films (< 2 nm)", *Tribology International* **81**, 73 (2015). Reprinted with permission from Elsevier. Copyright (2014).

In Chapter 5:

5. **R. J. Yeo**, N. Dwivedi, E. Rismani, N. Satyanarayana, S. Kundu, P. S. Goohpattader, H. R. Tan, N. Srinivasan, B. Druz, S. Tripathy, and C. S. Bhatia, "Enhanced tribological, corrosion, and microstructural properties of an ultrathin (< 2 nm) silicon nitride/carbon bilayer overcoat for high density magnetic storage", *ACS Applied Materials & Interfaces* **6**, 9376 (2014). Reprinted with permission. Copyright (2014) American Chemical Society.
6. N. Dwivedi, E. Rismani-Yazdi, **R. J. Yeo**, P. S. Goohpattader, N. Satyanarayana, N. Srinivasan, B. Druz, S. Tripathy, and C. S. Bhatia, "Probing the role of an atomically thin SiN_x interlayer on the structure of ultrathin carbon films", *Scientific Reports* **4**, 5021 (2014). Reprinted under the Creative Commons CC-BY-NC-SA 3.0 license.

In Chapter 6, Appendix B and Appendix C:

7. **R. J. Yeo**, N. Dwivedi, L. Zhang, Z. Zhang, C. Y. H. Lim, S. Tripathy, and C. S. Bhatia, "Durable ultrathin silicon nitride/carbon bilayer overcoats for magnetic heads: the role of enhanced interfacial bonding", *Journal of Applied*

Physics **117**, 045310 (2015). Reprinted with the permission of AIP Publishing. Copyright (2015).

8. **R. J. Yeo**, N. Dwivedi, S. Tripathy, and C. S. Bhatia, “Excellent wear life of silicon nitride/tetrahedral amorphous carbon bilayer overcoat on functional tape heads”, *Applied Physics Letters* **106**, 091604 (2015). Reprinted with the permission of AIP Publishing. Copyright (2015).

9. N. Dwivedi, **R. J. Yeo**, Z. Zhang, C. Dhand, S. Tripathy, and C. S. Bhatia, “Interface engineering and controlling the friction and wear of ultrathin carbon films: high sp^3 versus high sp^2 carbons”, *Advanced Functional Materials* **26**, 1526 (2016). Reprinted with permission. Copyright (2016) WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

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August 2015 Reuben Jueyuan Yeo

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Contents

Symbols and Abbreviations

@	At
$\sim$	Approximately
$<$	Less than
$>$	Greater than
$\leq$	Less than or equal to
°C	Degrees Celsius
°	Degrees (angle)
μm	Micrometer
0D	Zero-dimensional
1D	One-dimensional
2D	Two-dimensional
a.u.	Arbitrary units
A	Amperes
Å	Angstrom
a-C:H	Hydrogenated amorphous carbon
a-C:N	Nitrogenated amorphous carbon
a-C	Amorphous carbon
AES	Auger Electron Spectroscopy
AFM	Atomic Force Microscopy *or* Antiferromagnetic
AgCl	Silver chloride
Ag	Silver
Al_2O_3	Aluminum oxide
Al	Aluminum
AlTiC	Aluminum oxide/Titanium carbide composite
Ar	Argon
ASTC	Advanced Storage Technology Consortium
BaFe	Barium ferrite
BBSNR	Broad band signal-to-noise ratio
BE	Binding energy
Bi	Bismuth

BPM	Bit-patterned media
C	Carbon
CCD	Charge coupled device
cm	Centimeter
COC	Carbon overcoat
Co	Cobalt
CoCrPt	Cobalt chromium platinum
COF	Coefficient of friction
CoZrTa	Cobalt zirconium tantalum
Cr	Chromium
Cs	Caesium
CVD	Chemical vapor deposition
dB	Decibels
DC	Direct current
DLC	Diamond-like carbon
e.g.	For example
E_{oc}	Open circuit potential
eV	Electron-volts
FCVA	Filtered cathodic vacuum arc
Fe	Iron
FePt	Iron platinum
Gb	Gigabits
g	Grams
GMR	Giant magnetoresistance
GPa	Gigapascals
HAMR	Heat-assisted magnetic recording
HCA	Head cleaning agent
HDD	Hard disk drive
HDI	Head-disk interface
H	Hardness *or* Hydrogen
HiPIMS	High-power impulse magnetron sputtering
HMS	Head-media spacing
HRTEM	High resolution transmission electron microscopy
i.e.	That is to say
I	Current
I_D/I_G	D peak-to-G peak intensity ratio
IME	Institute of Microelectronics, Singapore
IMRE	Institute of Materials Research and Engineering, Singapore
in	Inches
INSIC	Information Storage Industry Consortium
I-V	Current–voltage
j_{corr}	Corrosion current density
k or k_B	Boltzmann constant
keV	Kiloelectron-volts
kHz	Kilohertz

K_u	Magnetic anisotropy constant
LTO	Linear Tape Open
min	Minutes
m	Meters
M	Molar (concentration) = mol/dm^3
MgO	Magnesium oxide
mN	Millinewtons
MOKE	Magneto-optical Kerr effect
MPa	Megapascals
MR	Magnetoresistance
MTJ	Magnetic tunnel junction
mTorr	Millitorr
mV	Millivolts
N_2	Nitrogen gas
nA	Nanoamperes
NiFe	Nickel iron *or* Permalloy
nm	Nanometers
N	Newtons (force) *or* Nitrogen
O	Oxygen
PECVD	Plasma enhanced chemical vapor deposition
PE	Protective efficiency
PFPE	Perfluoropolyether
PMR	Perpendicular magnetic recording
Pt	Platinum
PTR	Pole tip recession
PVD	Physical vapor deposition
R_a	Average roughness
RF	Radio frequency
RH	Relative humidity
RMS	Root-mean-square
R_q	Root-mean-square roughness
sccm	Standard cubic centimeters per minute
SEM	Scanning electron microscopy
Si_3N_4	Silicon nitride
SiN_x	Amorphous silicon nitride
Si	Silicon
SNR	Signal-to-noise ratio
sp^2C	sp^2-hybridized carbon
sp^3C	sp^3-hybridized carbon
SRIM	Stopping and range of ions in matter
s	Seconds
SUL	Soft underlayer
ta-C:H	Tetrahedral hydrogenated amorphous carbon
ta-C:N	Tetrahedral nitrogenated amorphous carbon
ta-C	Tetrahedral amorphous carbon

Ta	Tantalum
Tb	Terabits
TB	Terabytes
TFC	Thermal fly-height control
TiC	Titanium carbide
TiN	Titanium nitride
TMR	Tunneling magnetoresistance
TOF-SIMS	Time-of-flight secondary ion mass spectrometry
T	Temperature
UV	Ultraviolet
V	Volume *or* voltage
XPS	X-ray photoelectron spectroscopy
Ω	Ohms (electrical resistance)