Coverage and properties of *a*-SiN$_x$ hard disk overcoat

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Amorphous silicon nitride (*a*-SiN$_x$) overcoats are deposited on magnetic disks by rf-reactive sputtering to study their coverage and properties. According to the XPS analysis, *a*-SiN$_x$ has a low coverage limit of ~10 Å compared with that of the reference *a*-CN$_x$ (~20 Å). The lower coverage limit of *a*-SiN$_x$ may be attributed to its high density of 3.2 g/cm^3, which corresponds to 93% bulk density. By contrast, the density of DLC is only 54% that of diamond. This is in agreement with the results of coverage simulation, which reveal that the film coverage thickness decreases by ~3 Å per 10% increase in the relative density. Compared with 45 Å *a*-CN$_x$ coated disks, 15 Å *a*-SiN$_x$ coated disks have fewer pinhole defects and are more durable in the accelerated flyability test. The superior performance of *a*-SiN$_x$ disk overcoat may be attributed to its dense structure and high hardness (25GPa).

I. INTRODUCTION

Continuation of the rapid increase in the recording density of magnetic disks drives necessitates the reduction of magnetic spacing between the head and the magnetic disk. This can be partly achieved by reducing the thickness of the disk overcoat, which typically consists of diamond-like-carbon (DLC) deposited by sputtering or ion beam deposition (IBD).[1] For 1 Tb/in^2 recording density, the magnetic spacing would be 6.5 nm,[2] and the thickness of the disk overcoat would thus be less than 2 nm by scaling accordingly. However, a recent study has shown that the minimum thickness of DLC required to prevent the oxidation of the underlying CoPtCr layer is about 2 nm,[3] which represents a fundamental coverage limit for the DLC overcoat.

A previous study on amorphous silicon nitride (*a*-SiN$_x$) disk overcoat deposited by plasma-enhanced chemical vapor deposition (PECVD) has found *a*-SiN$_x$ to be hard and wear resistant.[4] In this paper we report on properties and performance of rf-reactively sputtered *a*-SiN$_x$ overcoat with an emphasis on its coverage limit on a thin-film magnetic recording disk. Aggressive flyability and pinhole-etch tests are carried out for disks coated with 15 Å thick *a*-SiN$_x$ and 45 Å thick reference *a*-CN$_x$ for comparison. The results show that *a*-SiN$_x$ not only has a lower coverage limit, but it also significantly outperforms thicker *a*-CN$_x$.

II. EXPERIMENTAL

Silicon nitride films were deposited using a BPS Circulus M12T static sputtering system equipped with radio frequency (rf) powered (13.56 MHz) cathodes. The base pressure of the sputtering chamber was less than 2 x 10^{-7} Torr. The rf-reactive sputtering process was carried out using Si targets (99.99% purity) in N$_2$/Ar atmospheres. Table I lists properties of *a*-SiN$_x$, the composition of which is essentially stoichiometric (Si$_3$N$_4$). For comparison purpose, properties of a reference *a*-CN$_x$ deposited by dc-reactive sputtering are also listed. Thin *a*-SiN$_x$ and *a*-CN$_x$ films were deposited on CoCrPt coated glass disks at 170-190 °C.

X-ray photoelectron spectroscopy (XPS) was used to study the coverage limits of *a*-SiN$_x$ and reference *a*-CN$_x$ overcoats because the surface of CoPtCr magnetic alloy would readily oxide and form a layer of metal oxide in ambient air without the adequate protection of the overcoat.[3] The procedures used in the present XPS analysis have been described elsewhere.[3] A recent study has also shown that the amount of lubricant bonded to the overcoat surface varies until reaching a critical thickness, beyond which the amount of bonded lubricant reaches a constant level and hence the overcoat exhibits a "bulk-like" behavior.[5] Following the procedures described in the aforementioned reference,[5] *a*-SiN$_x$ and reference *a*-CN$_x$ were titrated with Zdol 4000 lubricant as a function of the

Table I. Properties of *a*-SiN$_x$ and reference *a*-CN$_x$ overcoats.

Overcoat	N content (at.%) [a]	Density (g/cm^3) [b]	Hardness (GPa) [c]
a-SiN$_x$	56 ± 3	3.20 ± .05	25 ± 1
a-CN$_x$	10 ± 3	1.80 ± .05	11 ± 1

[a] N content is measured by Rutherford backscattering spectrometry from a 500-1000 Å thick film sample.
[b] density is determined by x-ray reflectivity from 500-600 Å thick film samples.
[c] hardness is determined by a MTS Nanoindenter from 1200 Å thick film samples.

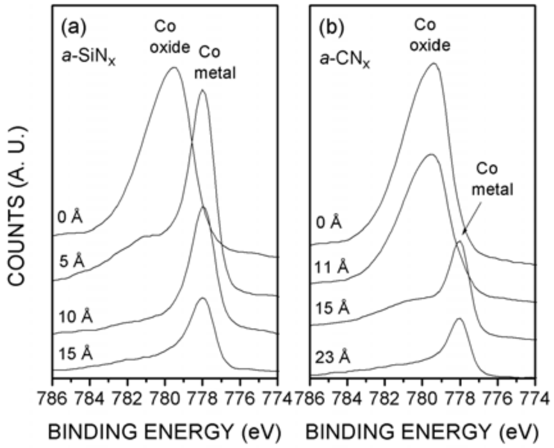

FIG. 1. XPS Co2*p* core level spectra of (a) *a*-SiN$_x$ coated and (b) *a*-CN$_x$ coated CoCrPt disks.

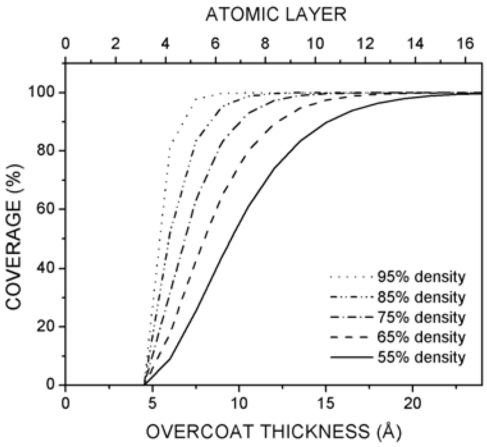

FIG. 2. Effect of overcoat thickness on coverage for various relative density values according to the simulation model described by Eq. (1).

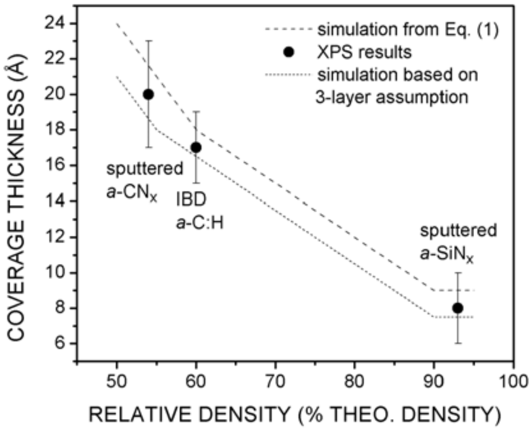

FIG. 3. Variation of overcoat coverage thickness with relative density according to simulation and XPS experiments.

overcoat thickness to determine their respective critical thicknesses. The pinhole defect density of the overcoat was determined by immersing the disk in an etchant (3% $Ce(NH_4)_2(NO_3)_6$ and 97% H_2O by weight) that attacks the underlying CoPtCr alloy. To evaluate the robustness of the head/disk interface, *a*-SiN$_x$ and reference *a*-CN$_x$ disks coated with 10 Å of a PFPE lubricant were subjected to an accelerated flyability test, which entails the flying of a head over a fixed track on the disk surface at a velocity of 19 m/s and at a sub-ambient pressure 25 kPa. The thickness of *a*-SiN$_x$ deposited on magnetic disks was verified by ellipsometry and specular x-ray reflectivity (XRR).[3]

III. RESULTS AND DISCUSSION

The XPS results in Fig. 1(a) show the evolution of the Co2*p* core level spectrum with the overcoat thickness for *a*-SiN$_x$ coated disks. The Co2*p* spectrum of the bare magnetic disk consists of a single peak at ~780 eV, which can be attributed to Co oxide. This suggests that 3-5 nm of Co oxide is formed on the surface of the CoPtCr without the overcoat protection. When 5 Å of *a*-SiN$_x$ is deposited on the CoPtCr surface, however, the intensity of the Co oxide peak decreases while a second peak at ~778 eV that corresponds to Co metal appears in the spectrum. The 5 Å thick *a*-SiN$_x$ overcoat provides some protection against oxidation in air as evidenced by the presence of the metal peak. As the thickness of *a*-SiN$_x$ is increased to 10 Å, the oxide peak completely disappears and only the metal peak remains in the Co2*p* spectrum, indicating that 10 Å of *a*-SiN$_x$ is sufficient to cover the underlying CoPtCr alloy and prevent the oxidation thereof. Further increase in the *a*-SiN$_x$ thickness does not alter the XPS Co2*p* core level spectrum, except for the decrease in the Co metal peak intensity because of the attenuation by thicker *a*-SiN$_x$.

Comparing with the XPS results of *a*-SiN$_x$ coated disks, Fig. 1(b) shows the XPS Co2*p* core level spectra for the reference *a*-CN$_x$ coated disks. Like the Co2*p* spectrum of the bare CoPtCr alloy, the spectrum of the 11 Å *a*-CN$_x$ exhibits only the metal oxide peak, indicating that 11 Å thick *a*-CN$_x$ does not provide any protection against oxidation in air. As its thickness increases to 15 Å, *a*-CN$_x$ begins to provide limited protection as evidenced by the presence of Co metal peak. The disappearance of oxide peak at 23 Å implies a complete coverage is attained. Hence, the minimum *a*-CN$_x$ thickness required for coverage can be estimated to be 20 Å, which is in agreement with a previous study.[3] Compared with *a*-CN$_x$, *a*-SiN$_x$ has a lower coverage limit of only 10 Å. This difference may be partly due to their respective densities. The density of *a*-SiN$_x$, 3.2 g/cm^3, corresponds to 93% bulk density of Si_3N_4. By contrast, the density of *a*-CN$_x$, 1.9 g/cm^3, is only equivalent to 54% bulk density of diamond.

To further investigate the effect of relative density, or the ratio of actual film density over theoretical density, on critical coverage thickness of overcoat, a statistic model of

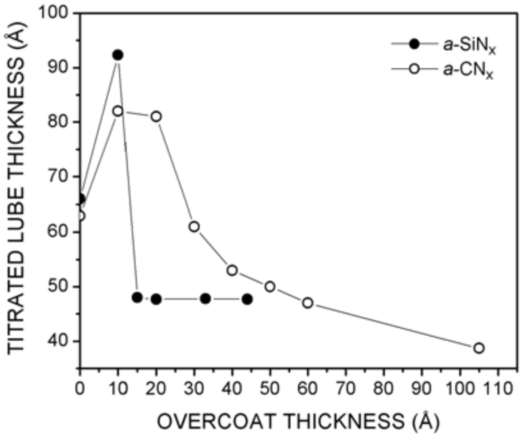

FIG. 4. Titrated Zdol 4000 thickness as a function of overcoat thickness for a-SiN$_x$ and a-CN$_x$ coated magnetic disks.

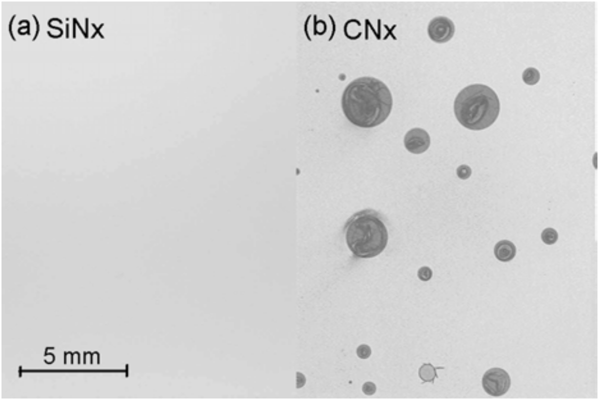

FIG. 5. Surfaces of CoPtCr disks coated with (a) 15 Å a-SiN$_x$ and (b) 45 Å a-CN$_x$ after 3 min etch in Ce(NH$_4$)$_2$(NO$_3$)$_6$ solution.

atomic layer growth is constructed and compared to the XPS results. First, the relative density of each atomic layer is assumed to be same as the overall relative density of the film. Second, it is assumed that four layers of atoms are needed to prevent the oxidation of CoPtCr surface with RMS roughness of 6-8 Å at 170-190 °C because of the lack of reference information and the complicated nature of Co oxidation involved. However, it will be shown later that this assumption does not markedly affect the final results. Based on these assumptions, the fraction of surface that is fully covered by at least four layers of atoms can be derived as

$$C = 1-(1-\rho)^{n} - n\rho(1-\rho)^{n-1} - \frac{n(n-1)}{2}\rho^{2}(1-\rho)^{n-2} - \frac{n(n-1)(n-2)}{6}\rho^{3}(1-\rho)^{n-3} \quad ,(1)$$

where ρ is the relative density of the film and n is the number of atomic layers. Assuming that each atomic layer has a thickness of 1.5 Å for small covalently bonded atoms, the coverage, C, is plotted as a function of the overcoat thickness according to Eq. (1) for different relative density values (Fig.2). The critical coverage thickness, defined here as the thickness at which $C \geq 0.99$, can then be plotted as a function of the relative density as shown in Fig. 3. The modeling results based on Eq. (1) are in good agreement with the XPS results, which also include that of an a-C:H film produced by ion beam deposition.[1] If the number of atomic layers required to prevent oxidation were 3 instead of 4, as initially assumed, the curve would simply move downward by 1.5 Å (Fig. 3). This, however, does not alter the main conclusion of the simulation—the required thickness for coverage decreases by ~3 Å with every 10% increase in the relative density.

The maximum quantity of Zdol lubricant that can be bonded to a-SiN$_x$ and a-CN$_x$ surfaces, or the "titrated" Zdol thickness, is plotted in Fig. 4 as a function of the overcoat thickness. As the a-SiN$_x$ thickness decreases from 15 to 10 Å, the titrated Zdol thickness increases owing to the effect of the underlying CoPtCr magnetic layer.[5] For a-SiN$_x$ thickness ≥ 15 Å, the titrated Zdol thickness remains constant and the film thus exhibits a "bulk-like" behavior. By contrast, a-CN$_x$ does not exhibit a clear threshold thickness although the titrated Zdol thickness drops precipitously at 30 Å. In general, the threshold thickness for sputtered a-C:H and a-CN$_x$ films determined by Zdol titration is ≥ 30 Å.[5]

Figure 5 shows the surfaces of 15 Å a-SiN$_x$ and 45 Å a-CN$_x$ coated disks after immersing in the Ce(NH$_4$)$_2$(NO$_3$)$_6$ solution for 3 minutes. The dark spots represent pinholes through which the etchant attacked the underlying CoPtCr magnetic alloy. While there is no visible pinhole on the a-SiN$_x$ disk, the surface of the reference a-CN$_x$ disk is covered by pinhole defects (~10/cm^2). Not only can 15 Å a-SiN$_x$ provides better corrosion protection, but the accelerated flyability test also reveals that 15 Å a-SiN$_x$ coated disks last longer than 45 Å a-CN$_x$ coated disks—180-360 min for a-SiN$_x$ versus 50-90 min for a-CN$_x$. The superior durability of a-SiN$_x$ may be attributed in part to its high hardness (Table I).

ACKNOWLEDGMENTS

The authors gratefully acknowledge Ms. D. C. Miller for the XPS analysis, Dr. A. J. Kellock for the RBS analysis, Drs. B. R. York and Q.-F. Xiao for the XRR analysis, and Dr. H. Deng for the flyability test.

[1] B. K. Yen, J.-U. Thiele, M. Geisler, P. H. Kasai, R. L. White, B. R. York, H. Zadoori, A. J. Kellock, W. C. Tang, T.-W. Wu, M. F. Toney, and B. Marchon, IEEE Trans. Magn. **37**, 1786 (2001).
[2] R. W. Wood, J. Miles, and T. Olson, IEEE Trans. Magn. **30**, 1711 (2002).
[3] C. M. Mate, B. K. Yen, D. C. Miller, M. F. Toney, M. Scarpulla, and J. E. Frommer, IEEE Trans. Magn. **36**, 110 (2000).
[4] Z. Kovac and V. J. Novotny, IEEE Trans. Magn. **27**, 5071 (1991).
[5] R. J. Waltman, H. Zhang, A. Khurshudov, D. Pocker, M. A. Karplus, B. York, Q.-F. Xiao, H. Zadoori, J.-U. Thiele, G. W. Tyndall, Trib. Lett. **12**, 51 (2002).