Probing the Role of an Atomically Thin SiNₓ Interlayer on the Structure of Ultrathin Carbon Films

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Filtered cathodic vacuum arc (FCVA) processed carbon films are being considered as a promising protective media overcoat material for future hard disk drives (HDDs). However, at ultrathin film levels, FCVA-deposited carbon films show a dramatic change in their structure in terms of loss of sp³ bonding, density, wear resistance etc., compared to their bulk counterpart. We report for the first time how an atomically thin (0.4 nm) silicon nitride (SiNₓ) interlayer helps in maintaining/improving the sp³ carbon bonding, enhancing interfacial strength/bonding, improving oxidation/corrosion resistance, and strengthening the tribological properties of FCVA-deposited carbon films, even at ultrathin levels (1.2 nm). We propose the role of the SiNₓ interlayer in preventing the catalytic activity of Co and Pt in media, leading to enhanced sp³C bonding (relative enhancement ~40%). These findings are extremely important in view of the atomic level understanding of structural modification and the development of high density HDDs.

Ultrathin diamond-like carbon (DLC) films are widely used in the hard disk drives (HDDs) industry to protect the surface of hard disk media and head from corrosion and mechanical wear. With the continuously increasing demands of inexpensive and small HDDs, the areal density of these drives is increasing at a rate of 20–30% annually. The reduction of magnetic spacing, which is the vertical distance between the magnetic layer in media and magnetic elements in the head, is one of the most important parameters to achieve high areal density as Wallace had proposed that the readback signal increases exponentially with decreasing magnetic spacing. It has been reported that a carbon overcoat (COC) of ~2.5 nm is required to obtain an areal density of ~1 Tb/in². In order to advance beyond 1 Tb/in², the COC thickness has to be reduced. Currently, plasma enhanced chemical vapor deposition (PECVD) grown hydrogenated carbon (CHₓ) overcoats (OCs) are used on commercial media disks. However, the reduction of the current commercial COCs thickness below 2 nm may introduce many corrosion and tribological challenges. Recently, heat-assisted magnetic recording (HAMR) – which employs a highly focused and intense laser beam to help lower the coercivity, momentarily, of the media to allow recording of information on it – has gained enormous scientific and industrial attention for future high density HDDs. Since the laser beam also interacts with COC, the performance of current commercial COC is degraded due to its thermal instability. In order to obtain better corrosion and wear protection at low COC thicknesses while keeping HAMR application in mind, alternative techniques for the development of COC on media have to be explored.

The FCVA technique, which has the ability to produce highly dense and continuous carbon films even at a thickness level of ~2 nm, has opened up possibilities for creating next generation high areal density HDDs. It produces a highly ionized (~90%) plasma of carbon ions which have an average energy of ~20–25 eV. These carbon ions strike the substrate and produce a smooth, continuous, highly dense and high sp³ bonded carbon film. The continuous and dense structure of FCVA-deposited carbon films is important for protecting the magnetic hard disk media against corrosion/oxidation, while the high sp³ carbon (sp³C) bonding characteristic within the film offers excellent resistance against mechanical wear. Moreover, given its high thermal stability property, FCVA-deposited carbon has been considered as an ideal COC for HAMR application.

However, it has been reported that a reduction of the thickness of FCVA-deposited carbon also introduces dramatic structural changes, such as lowering the sp³C bonding as compared to its bulk counterpart. Robertson and Chhowalla et al. suggested that thicker carbon films of 50 nm and above grown using FCVA (also referred
to as tetrahedral amorphous carbon or ta-C) could have high sp$^3$C bonding in the range of 80–90%. However, Zhang and Komvopoulos$^{12}$ have observed sp$^3$C bonding in the range of 20–50% in FCVA carbon modified hard disk media samples, where the carbon film thickness was only 2–3 nm. Begoš et al.$^{13}$ performed in-depth investigations of the bonding of FCVA-grown carbon films as a function of thickness and found that both sp$^3$ bonding and density were reduced with decreasing thickness below 10 nm. Still, Ferrari$^{14}$ suggested that FCVA-deposited carbon films could have sp$^3$C bonding of ~50% even at a thickness of 2 nm, which is considerably higher than sputtered and PECVD-based carbon films of the same thickness. As next generation high density HDDs require COGs with thickness of 1–2 nm or even less with their high thermal stability and protective characteristics, FCVA-deposited carbon seems to be a potential candidate as a COC for future HDDs. However, its structural properties – mainly the sp$^3$C bonding at the thickness level of 1 to 2 nm – have to be maintained or improved. Hence, new approaches, processes and structural designs of media disk OCs have to be proposed and executed.

Silicon nitride (Si$_N$) has a high atomic density and is being considered in the magnetic storage industry as an alternative material for COC on media$^{15,26}$. However, as a single overcoat, Si$_N$ suffers from poor tribological performance and oxidation$^{15,26}$. Nevertheless, when used together, the Si$_N$ and FCVA-deposited carbon in one structure may show promising properties due to their synergistic effect. Recently, Bunnak et al.$^{27,28}$ prepared composite Si$_N$/DLC films by the FCVA (for DLC) and radio frequency (RF) sputtering (for Si$_N$) techniques, and found that Si$_N$/DLC films revealed better structural and mechanical properties than single-layer DLC. However, their work investigated 10 nm thick films, which is far beyond the current thickness requirement of COC on magnetic storage media. Hence, the grand challenge is to maintain the better structural properties of FCVA-deposited carbon at the thickness of 1–2 nm.

In this work, we explore the structural properties of ultrathin carbon films grown with and without the silicon nitride (Si$_N$) interlayer. The understanding of how the application of an atomically thin Si$_N$ (0.4 nm) interlayer influences the interfacial bonding and structure of ultrathin carbon films lies at the core of this study. Given their ability to probe the structure of ultrathin DLC films, Raman spectroscopy and X-ray photoelectron spectroscopy (XPS)$^{29–48}$ are employed as spectroscopic characterization tools for structural analysis.

**Results**

Fig. 1 displays the cross-sectional schematic of a 2.5″ commercial hard disk media (CM3a) sample used in this work. A commercial hard disk typically contains a seed layer grown on a glass substrate, above which many magnetic layers are deposited, such as the soft underlayer 1 (SUL 1), antiferromagnetic (AFM) coupling layer, SUL 2, intermediate layer 1, intermediate layer 2, and finally, the magnetic storage layer of CoCrPtOxide on top. Above the magnetic storage layer, a 1–2 nm thick layer of commercial COC followed by a ~1 nm lubricant (lube) layer are deposited to protect the magnetic media from corrosion and wear. Figs. 1b–1g schematically illustrates the deposition process of the ultrathin FCVA-based carbon films with and without the Si$_N$ interlayer. To grow these films, the commercial COC and lube had to be removed first. Hence, the etching of commercial COC and lube of CM3a was conducted in an ion beam etch chamber using Ar$^+$ ions at ion energy of 300 eV (Figs. 1c and 1d), followed by the transferring of the etched CM3a samples in the FCVA chamber under high vacuum conditions. The reason for applying this etching step of *in-situ* overcoat removal is to perform the growth of carbon films on an oxide-free surface of magnetic media. The deposition of ultrathin carbon films was done on etched hard disk media samples using the FCVA process.

Two runs were performed on two separate batches of the samples after etching to obtain single-layer FCVA-deposited carbon films of thicknesses ~1.2 nm (CM3a/12C) and ~1.6 nm (CM3a/16C) (Fig. 1e). A third run was performed to fabricate the Si$_N$/carbon bilayer structure (CM3a/4SiN12C) with Si$_N$ as an interlayer. An atomically thin Si$_N$ layer of ~0.4 nm was first deposited on the etched media surface using pulsed direct current (DC) reactive sputtering of Si target with a gaseous mixture of Ar and N$_2$ (Fig. 1f), followed by the deposition of a ~1.2 nm carbon film by FCVA (Fig. 1g). The description of all the samples used in this work is given in Table 1.

**Transmission electron microscopy (TEM).** The thicknesses of the FCVA-deposited carbon films with and without the Si$_N$ interlayer...
as well as the specially prepared commercial media sample with commercial COC but no lube (sample CMC) were measured using high resolution cross-section TEM, as shown in Figs. 2a–2d. The thicknesses of the different OCs can be estimated between the capping layer and the magnetic layers. It is evident from Fig. 2a that the thickness of commercial COC in sample CMC was found to be 2.7 ± 0.1 nm. On the other hand, the thicknesses of the FCVA-deposited carbon films in samples CM3a/12C and CM3a/16C (Figs. 2b and 2c) were measured to be ~1.2 ± 0.1 nm and ~1.6 ± 0.1 nm, respectively, which matched with our calibration. Lastly, the OC thickness in sample CM3a/4SiN12C was also measured to be ~1.6 ± 0.1 nm. Due to the similar contrast of SiNₓ and carbon observed in the TEM image, coupled with the atomic level thickness (~0.4 nm) of SiNₓ which could possibly have been intermixed with carbon, it is difficult to distinguish between the two layers from the TEM cross-sectional image of this sample in Fig. 2d. However, the angle resolved X-ray photoelectron spectroscopy (ARXPS) results (discussed later) revealed the presence of the SiNₓ interlayer in the CM3a/4SiN12C sample. The thickness of the overcoats measured by TEM matches well with the calibrated deposition rate, which was carried out by X-ray reflectivity (XRR) measurements. Details are given in the methods section.

Further, while analyzing the TEM images, we found that FCVA-deposited carbon in sample CM3a/12C showed a formation of nanocrystalline layered structure. The 1.2 nm COC comprised few atomic layers and deposited onto the CoCrPt-alloys based media. The Co and Pt, which are transition metals, are active catalyst and may assist to form the nanostructured morphology in carbon due to catalytic activity. These nanostructures may be rich in sp² bonding and clustering, thus this sample should possess relatively lesser sp³ bonding, which as explained in discussion section. However, the layered structure was relatively reduced in samples CM3a/16C and CM3a/4SiN12C. This may be due to the increase in sp³ bonding and reduction in the catalytic activity of the Co and Pt atoms because of an increase in the carbon thickness and introduction of 0.4 nm SiNₓ interlayer respectively, which are explained in discussion section. In contrast, lesser or negligible layering of carbon was observed in a TEM image of sample CMC.

**Angle resolved X-ray photoelectron spectroscopy (ARXPS).** ARXPS, utilizing different grazing angles for surface analysis, can effectively probe the chemical bonding and structure of ultrathin films and interfaces. Hence, detailed analyses of the chemical structure, composition and oxidation/corrosion resistance of these samples were performed using ARXPS. Each of the high resolution spectra was recorded under varied photoelectron take-off angles (TOA) from 15° to 65° (90° being normal to the surface). Figs. 3a–3c show the C 1s, Co 2p 3/2 and Cr 2p core level spectra of sample CM3a/12C, while Figs. 3d–3h display the C 1s, Co 2p 3/2, Cr 2p Si 2p and N 1s core level spectra of sample CM3a/4SiN12C. At a TOA of 15°, the signal came mainly from the topmost surface giving a strong C 1s peak, and weaker Co 2p 3/2 and Cr 2p core level spectra of sample CM3a/12C, while Figs. 3d–3h display the C 1s, Co 2p 3/2, Cr 2p Si 2p and N 1s core level spectra of sample CM3a/4SiN12C. At a TOA of 15°, the signal came mainly from the topmost surface giving a strong C 1s peak, and weaker Co 2p 3/2 and Cr 2p Si 2p and N 1s peaks in sample CM3a/12C and CM3a/4SiN12C. The intensity of the Co 2p 3/2 and Cr 2p peaks in both of these samples as well as the intensity of the Si 2p and N 1s peaks in sample CM3a/4SiN12C were found to rise continuously with increasing TOA from 15° to

### Table 1 | Nomenclature and description of different samples used in present work

| Nomenclature | Sample Description |
|--------------|--------------------|
| CMb          | Specially prepared commercial magnetic media disk without COC and lube. |
| CMC          | Specially prepared commercial magnetic media disk with its original COC (~2.7 nm) but no lube. |
| CM3a/12C     | Overcoats etched CM3a containing ultrathin a-C film (~1.2 nm) grown using FCVA. |
| CM3a/16C     | Overcoats etched CM3a containing ultrathin a-C film (~1.6 nm) grown using FCVA. |
| CM3a/4SiN12C | Overcoats etched CM3a containing atomically thin SiNₓ interlayer (0.4 nm) by pulsed DC reactive sputtering, followed by deposition of ultrathin a-C film (~1.2 nm) using FCVA. |

**Figure 2 | Cross-sectional TEM analysis for determination of the thickness and the structure of carbon films.** TEM images of samples (a) CMC, (b) CM3a/12C, (c) CM3a/16C and (d) CM3a/4SiN12C.
65°. This is due to the TOA having a steeper angle with respect to the surface as the angle increases, which analyzes the photoelectrons that are emitted deeper beneath the surface, nearer to the interface and media. This relation, however, does not hold for the C 1s core level spectra. With increasing TOA from 15° to 25°, the intensity of the C 1s peak for both spectra rose due to a high carbon signal from the surface, but beyond TOA of 25°, no relation between the intensity of the C 1s peak and TOA was observed as the TOA approached the interface and media. Since the C 1s peak positions at the lowest and highest TOAs of 15° and 65° were found to be almost at the same binding energy position and the maximum intensities of the Co 2p_{3/2} and Cr 2p_{3/2} peaks were observed at TOA of 65°, the spectra corresponding to the TOA of 65° were considered for detailed structural, compositional and oxidation analyses of both samples. Moreover, the XPS spectra of samples CMC and CM3a/16C (not given in Fig. 3) were also recorded at a TOA of 65° ± 2° for analysis and comparison. Additionally, it should be noted that the Si and N peaks (shown in Figs. 3g and 3h) became prominent at TOA of 35° as compared to 15° and 25°, due to the higher probability of escaping photoelectrons close to the interface region at this TOA. Hence, the Si 2p and N 1s spectra taken at TOA of 35° were also considered for interface bonding and other analyses, apart from their spectra at TOA of 65°.

The Co 2p_{3/2} spectra of samples CMb, CMC, CM3a/12C, CM3a/16C and CM3a/4SiN12C are compared in Figs. 4a–4e, whereas their Cr 2p_{3/2} spectra are compared in Figs. 4f–4j. Sample CMb was specially prepared bare magnetic media with a magnetic storage layer of CoCrPt-oxide on top (i.e. no COC and no lube). It is evident from Fig. 4a that CMb showed a very minor peak at ~778.1 eV corresponding to the metallic state of Co, but a very broad and intense major peak at ~780.5 eV assigned to the oxide state of Co. This implies that Co in CMb without any surface protection exists mainly in the oxidized state. Similarly, the Cr 2p_{3/2} peak in CMb centered at ~576.0 eV was found to be very broad, indicating that Cr also exists mainly in the oxidized state. When OCs were deposited over the magnetic media, the Co 2p_{3/2} and Cr 2p_{3/2} peaks were observed at ~778.1 eV and ~574.0 ± 0.2 eV respectively, in samples CMC, CM3a/12C, CM3a/16C and CM3a/4SiN12C. This indicated that all the OCs, whether the thicker commercial COC (~2.7 nm) or thinner OCs with FCVA-deposited carbon, provide protection against oxidation/corrosion for the underlying magnetic storage layer. It is interesting to note that FCVA-deposited carbon, even at the thickness levels of 1.2 nm and 1.6 nm with and without the SiNx interlayer, provides considerably higher protection against oxidation/corrosion.

In order to examine the interfacial and bulk bonding of various elements, the C 1s, Co 2p_{3/2}, Cr 2p_{3/2}, Si 2p and N 1s core level spectra of various samples taken at TOA of 65° were analyzed and compared in Figs. 5a–5n. The C 1s spectra of samples CMC, CM3a/12C, CM3a/16C, and CM3a/4SiN12C were fitted with four to five Gaussian components (Figs. 5a–5d), the Co 2p_{3/2} spectra were fitted with four to five Lorentzian-Gaussian components (Figs. 5e–5h), and the Cr 2p_{3/2} spectra were fitted with five Gaussian components (Figs. 5i–5l). The C 1s core level spectra of all samples showed four peaks #1, #2, #3

![Figure 3](https://www.nature.com/scientificreports)
Co$_2$O$_3$), Co-oxide/hydroxide (such as CoO, Co$_3$O$_4$, CoOOH or Co(OH)$_2$) and Co-oxide (cobalt oxide as in Co$_2$O$_3$), Co-oxide/hydroxide (such as CoO, Co$_3$O$_4$, CoOOH or Co(OH)$_2$) and Co-oxide/hydroxide (such as CoO, Co$_3$O$_4$, Co(OH)$_2$), respectively. Again, a fifth peak (#5) was observed only in CM3a/4SiN12C, respectively. Out of these five peaks, four peaks in the Si 2p spectrum were similar to that observed at TOA of 65° but with a slight change in their peak positions. The additional peak #5 in the Si 2p spectrum recorded at TOA of 35° was found to be at 103.3 eV, which is assigned to Si = O bonding$^{25}$. Likewise, out of the seven peaks in the N 1s core level spectrum, five peaks were similar to those observed at TOA of 65° but with a small shift in their peak positions. Additionally, a fifth peak (#5), which was obtained at 403.1 eV, can be assigned to NO$_x$ bonding$^{31,32}$. We have also deconvoluted and analyzed the Si 2p and N 1s core level spectra recorded at TOA of 35° with five and seven Gaussian components to obtain the best fit to the data, as shown in Figs. 5o and 5p. The percentages of the constituent peaks in all the core level spectra obtained for all samples were determined by an area ratio method and are shown in Fig. 6. The total sp$^3$C bonding in samples CMC and CM3a/12C was found to be ~33% in both; however, it continuously increased to ~37% and ~46.3% in samples CM3a/16C and CM3a/4SiN12C, respectively. Comparing the sp$^3$C bonding of sample CM3a/4SiN12C with sample CM3a/16C (while keeping total thickness constant at ~1.6 nm), an absolute increase of ~9.3% (relative increase of ~25%) in sp$^3$C bonding was observed in sample CM3a/4SiN12C. Similarly, comparing the sp$^3$C bonding of sample CM3a/4SiN12C with sample CM3a/12C (while keeping the carbon thickness constant at ~1.2 nm), an absolute increase of ~13.3% (relative increase of ~40%) in sp$^3$C bonding was observed in sample CM3a/4SiN12C. The increase in sp$^3$C bonding can thus be related to a SiN$_x$-induced change in the structure of the FCVA-deposited carbon film.

Figure 4 | Revealing the extent of oxidation/corrosion of Co and Cr in CMb and improvement of oxidation/corrosion resistance after application of COCs. The XPS core level spectra of (a)–(e) Co 2p$_{3/2}$ and (f)–(j) Cr 2p$_{3/2}$ for samples CMb, CMC, CM3a/12C, CM3a/16C and CM3a/4SiN12C recorded at TOA of 65°.
From the Co 2p 3/2 core level spectra, the metallic Co-Co/Co-Oxide (Co oxide/hydroxide) bonding fractions in samples CMC, CM3a/12C, CM3a/16C and CM3a/4SiN12C were also estimated and found to be ~68% (~32%), ~63% (~37%), ~62% (~38%) and ~78% (~22%), respectively. Likewise, from the Cr 2p 3/2 core level spectra, Cr-Cr/Cr2N (Cr oxide/hydroxide) bonding fractions in these samples were found to be ~76% (~24%), ~77% (~23%), ~79% (~21%) and ~79% (~21%), respectively. These findings indicate that the introduction of an atomically thin SiN x interlayer in carbon helps in enhancing (lowering) its sp 3C (sp2C) bonding, reducing Co oxidation and maintaining/reducing Cr oxidation, as compared to carbon films without a SiN x interlayer and thicker commercial COC. The details of the peak positions, associated bonding and the percentages of the constituent peaks of all the core level spectra obtained for all the samples are summarized in Table S1.1–S1.6 under supplementary information.

Micro-Raman Spectroscopy. Raman spectroscopy is a very promising tool for structural characterization of DLC films. The visible (488 nm) and ultraviolet (UV, 325 nm) Raman spectra of samples CMC, CM3a/12C, CM3a/16C and CM3a/4SiN12C are shown in Figs. 7a–7h. The Raman spectra of all samples were fitted...
with two Gaussian components. The visible Raman spectra showed two bands centered in the range of ~1565–1580 cm\(^{-1}\) (G band) and ~1380–1405 cm\(^{-1}\) (D band). However, when excited with UV light, the Raman spectra showed an additional band centered in the range of ~1050–1100 cm\(^{-1}\) (T band), in addition to the D and G bands centered in the range of ~1400–1420 cm\(^{-1}\) and 1580–1590 cm\(^{-1}\), respectively. The G peak corresponds to the symmetrical \(E_{2g}\) vibrational mode in graphite-like sp\(^2\) material and arises from the bond stretching motion of all pairs of sp\(^2\) atoms in both rings and chains against the restoring force\(^{32}\). The D peak corresponds to the \(A_1\), breathing mode of phonons near the zone boundary and appears in the presence of disorder caused by sp\(^2\) atoms in the rings\(^{33}\). Hence, both D and G peaks are associated with sp\(^2\)C bonding. On the other hand, the T peak which appears in UV excitation can be used for probing sp\(^3\)C bonding. Since the T peak in UV excitation was significantly less intense, we could not fit this peak in the Raman spectra.

For the visible Raman spectra as shown in Figs. 7a–7d, the exact G peak position in sample CMC was found to be at 1569.0 cm\(^{-1}\). However, the G peak position in the FCVA-deposited carbon samples CM3a/12C, CM3a/16C and CM3a/4SiN12C was found to be at 1575 ± 1 cm\(^{-1}\). In contrast, the G peak positions in samples CMC, CM3a/12C, CM3a/16C and CM3a/4SiN12C were found to be at 1582.0 cm\(^{-1}\), 1582.0 cm\(^{-1}\), 1586.0 cm\(^{-1}\) and 1588.0 cm\(^{-1}\), respectively, in the UV Raman spectra (Figs. 7e–7h). Robertson\(^4\) has reported that CH\(_x\) films with ~30% sp\(^3\)C bonding show a G peak close to 1570 cm\(^{-1}\) in visible Raman spectra. In the present case, sample CMC with CH\(_x\) OC by PECVD showed a G peak at 1569 cm\(^{-1}\) during visible excitation and possessed sp\(^3\)C fraction of ~33% (by ARXPS), corroborating with Robertson’s results\(^4\). For the present FCVA-deposited carbon films, the visible Raman spectra showed that the G peaks were almost at the same position. However, the UV Raman spectra showed a gradual shift in the G peak position from 1582 cm\(^{-1}\) to 1586 cm\(^{-1}\) to 1588 cm\(^{-1}\) for samples CM3a/12C, CM3a/16C and CM3a/4SiN12C, respectively. Ferrari and Robertson\(^{34}\) suggested that for FCVA-deposited carbon films undergoing UV excitation, an increase in the G peak position towards higher wavenumbers corresponds to an increase in sp\(^3\)C bonding. Hence, following the model by Ferrari and Robertson\(^{34}\) and our ARXPS results, it can be concluded that the carbon film on CM3a/4SiN12C contained the highest sp\(^3\)C bonding among all the samples. The I\(_D\)/I\(_G\) ratio, which is related to sp\(^2\) clustering, was also estimated and found to be 0.6, 0.7, 0.5 and 0.4 in samples CMC, CM3a/12C, CM3a/16C and CM3a/4SiN12C respectively, for visible excitation. No significant difference in the I\(_D\)/I\(_G\) ratio was observed among the samples for UV excitation, which varied between 0.7 and 0.8. This is due to the fact that visible Raman is predominantly sensitive to sp\(^2\)C bonding and clustering, whereas the UV Raman signal contains information about sp\(^3\)C bonding, in addition to sp\(^2\)C bonding. Therefore, the observed change in the G peak positions and I\(_D\)/I\(_G\) ratios can be attributed to the change in the micro-structure of OCs in terms of sp\(^2\)C and sp\(^3\)C bonding, sp\(^2\) clustering, their domain size and interfacial bonding, etc. In addition, a small T peak was visible in the UV Raman spectrum of sample CM3a/4SiN12C, as seen in Fig. 7h. This peak was slightly more intense than those for the other samples (Figs. 7e–7g) due to the presence of comparatively more sp\(^3\)C bonding, which has also been confirmed earlier by ARXPS.

**Discussion**

High sp\(^3\)C bonding – which improves the wear resistance and density, and enhances the oxidation/corrosion resistance – is the key characteristic of FCVA-deposited carbon films. However, these films show a dramatic change in their structure in terms of loss of sp\(^3\)C bonding when the thickness is reduced from bulk to ultrathin film levels. Efforts have been made to maintain/improve the sp\(^3\)C bonding, improve the interfacial bonding/strength, and enhance other associated properties by manipulating the structure through the introduction of an atomically thin SiNx interlayer. In terms of improving interfacial bonding, SiNx forms two interfaces when sandwiched between the COC and media, namely the upper interface at SiNx/C and the bottom interface at CoCrPt-Oxide/SiNx. At the bottom interface, interactions of Co with Si, and Cr with N form Co-Si (silicide) and Cr-N bonding, respectively. At the top interface, interactions of Si with C, and N with C give rise to strong Si-C and C-N (both sp\(^2\)C-N and sp\(^3\)C-N) bonding, as confirmed by the ARXPS analysis. Thus, the enhancement in the interfacial bonding with strong bonds, owing to the introduction of the SiNx interlayer, improves the interfacial strength significantly. These further help to enhance the adhesion of overcoat with underlying media and improve the wear resistance and frictional properties.
Within the carbon layer of different overcoats, the I_D/I_G ratio is the measure of sp^2 clustering and the formation of number of aromatic rings within the clusters. The I_D/I_G ratio varies directly with sp^2 cluster size and the number of aromatic rings. As shown by higher I_D/I_G ratio (0.7), the thinner FCVA deposited carbon such as 1.2 nm COC in sample CM3a/12C had tendency to form a significant amount of aromatic rings and sp^3 clusters, and at the same time showed larger sized sp^2 clusters within the sp^2 and sp^3 bonded carbon system. However, when the thickness of COC was increased to 1.6 nm in sample CM3a/16C, the I_D/I_G ratio decreased to 0.5, suggesting that an increase in thickness prevented the sp^2 clustering and aromatic ring formation, and lowered the size of sp^2 clusters. However, when the atomically thin 0.4 nm SiN_x interlayer was deposited below the 1.2 nm thick COC, the I_D/I_G ratio in sample CM3a/4SiN12C was further reduced to 0.4, indicating that the SiN_x interlayer has a great role in lowering the size of sp^2 clusters and preventing the formation of aromatic rings and sp^2 clusters within the sp^2 and sp^3 bonded carbon network. We have also recorded Raman spectra of these samples using 514 nm excitation to examine the nature of sp^2 clustering and found similar trend as observed with 488 nm excitation (see Supplementary section S3). Overall, the introduction of a SiN_x interlayer below the COC was found to increase the sp^3 bonding, lower the size of sp^2 clusters and decrease the amount and number of aromatic rings and sp^3 clustering within the carbon layer.

Why does an atomically thin SiN_x interlayer help in maintaining/improving sp^3 bonding? To understand this, we discuss the growth mechanism of FCVA-deposited carbon on media samples. In samples CM3a/12C and CM3a/16C, carbon is deposited directly over the CoCrPt/Oxide-media layer. It should be noted that the introduction of metals in DLC films promotes sp^2 bonding^35–37. Tristaris et al.^38 performed a detailed theoretical study on metal incorporated DLC films and found that the introduction of metals promotes sp^2 bonding mainly at the metal/carbon interface. Both Co and Pt are the transition metals having high adsorption characteristics and are considered as excellent catalysts. As evidence of this, recently, Pohl et al.^39 performed a study on FePt/carbon interfaces and found that FePt catalyzed the formation of carbon nanotubes (CNTs), which

Figure 8 | Schematic illustration of catalytic effect of Co and Pt on interfacial carbon, and how the catalyst effect becomes reduced upon the introduction of an atomically thin SiN_x interlayer. (a) Granular CoCrPt/Oxide storage layer, (b) direct deposition of ultrathin carbon film (in grey color) on the granular media by FCVA, and (c) generation of sp^2-rich interfacial carbon layer (in blue color) due to the catalytic influence of Co and Pt atoms. Figure (d) shows the deposition of a 0.4 nm SiN_x layer (in orange color) on the granular media followed by (e) deposition of an ultrathin carbon film by FCVA. The application of the SiN_x interlayer prevents the catalytic effect on FCVA-deposited carbon at the interface (f) and maintains/improves its sp^3 bonding.
have the sp² bonded structure. Bethune et al. also reported that Co catalyzed the formation of sp² bonded graphite-like structures around the Co clusters. In our case, since the 1.2 nm and 1.6 nm carbon films were extremely thin (comprising just a few atomic layers), we expect the direct interaction of FCVA-deposited carbon with Co and Pt in the media, which promotes sp³C bonding mainly at the interface region due to the catalytic effect. Moreover, by analyzing the TEM images, we observed the formation of a nano-crystalline layered structure in the CM3a/12C sample, which may be rich in the sp² phase mainly at the interface. This explains why a lower sp²C bonding with a fraction of ~33% was observed in sample CM3a/12C. When the thickness of FCVA-deposited carbon was slightly increased to 1.6 nm, the interfacial thickness remained similar, creating the same amount of sp³C bonding but the bulk thickness increased by ~0.4 nm. This explains why a slightly higher sp³C bonding of ~57% was observed in CM3a/16C. The catalytic nature of Co and Pt arises from the fact that FCVA-based carbon ions with energy of ~20–25 eV considerably raise the local temperature, referred to as localized heating, upon bombardment onto the CoCrPt-Oxide-media layer. At the same time, Co and Pt atoms lying at the media/carbon interface reduce the activation energy for chemical reactions to be occurring that promote the sp² phase of carbon without affecting the total energy required for the product. Hence, amorphous carbon when reacting with Co and Pt atoms transform into the sp²-rich phase at relatively low temperatures. Weimansetal. suggested that carbon ions with energy of 100 eV can heat up a region of 0.75 nm to a local temperature of ~3823 K. The carbon ion energy of 20–25 eV is also sufficient to heat up the substrate locally. Following this assumption, it is possible for the catalytic effect in our case to reach up to ~30–40% of the total film thickness. Thus this region, which can be referred to as the active carbon region, could experience higher sp³C bonding and clustering.

However, when the SiNₓ interlayer was introduced between the 1.2 nm FCVA-deposited carbon film and the CoCrPt-Oxide-media layer, the sp³C bonding decreased to 29.6%, leading to drastic stress at the interface due to an interfacial mismatch between the amorphous carbon when reacting with Co and Pt atoms transform without affecting the total energy required for the product. Hence, the increase in stress, to some extent, imposes pressure on the CoCrPt-Oxide-media layer. At the same time, Co and Pt atoms lying at the media/carbon interface reduce the activation energy for chemical reactions happening in the direct path of carbon ions. Thus, the introduction of a SiNₓ interlayer minimizes the degradation of sp³C bonding at both interfaces owing to the introduction of a SiNₓ interlayer reduce the metal-induced transformation of sp³ → sp² bonding. The schematic view of the Co- and Pt-induced catalytic effect on FCVA-deposited carbon, and how the SiNₓ interlayer minimizes the degradation of sp³C bonding are illustrated in Fig. 8. We also predict that the introduction of the SiNₓ interlayer might increase stress at the interface due to an interfacial mismatch between the carbon atoms and Si, which is confirmed by the shift of the G peak towards higher wavenumbers during the UV Raman analysis of these samples. Friedman and Sullivan as well as Wang and Komvopoulos have also reported that the interaction of carbon ions with silicon can increase the compressive stress at the SiC interface. Thus, the increase in stress, to some extent, imposes pressure on the system to lower the Gibbs free energy of sp³C bonding and hence, this could have led to the increase in sp³C bonding in sample CM3a/4SiN12C. We also performed tribological and electrochemical corrosion measurements on these samples and results are reported in supplementary information (Supplementary Figs. S2.1, S2.2 and S2.3). We observed that sample CM3a/4SiN12C performed well in terms of having high wear resistance, a lower coefficient of friction and high oxidation/corrosion resistance as compared to the other FCVA-deposited COCs and commercial COC. This could be due to the SiNₓ-induced strong interfacial bonding and improved sp³C bonding of carbon films.

In summary, by introducing an atomically thin SiNₓ interlayer to the designed overcoat structure, we have been able to maintain/increase the sp³C bonding, improve the adhesion of overcoat with underlying media and maintain/improve other associated properties of ultrathin carbon films such as low friction, high wear and oxidation/corrosion resistance. These findings are extremely important towards the realization of thin yet protective overcoats for high density magnetic storage media.

**Methods**

**Sample fabrication.** For comparison and investigation, five different types of samples were included in the present work, as described in Table 1. Sample CMb was bare magnetic media with neither COC nor lube, and CMG was commercial media with commercial COC (~2.7 nm) but without lube. The deposition of carbon films for CM3a/12C, CM3a/16C and CM3a/4SiN12C was performed in situ on etched CM3a media by FCVA (Veeco Instrument Inc.) at a carbon ion energy of ~20–25 eV (without intentional substrate biasing). The FCVA system was equipped with single 90° bend filter and high current pulsed power supply. During deposition of carbon by FCVA, pulsed power was applied to the target. Prior to final deposition, the calibration of the deposition rate was performed using XRR technique. We have calibrated the deposition thickness as a function of number of pulses applied to the target. The dose rate calibrated by the XRR was found to be ~0.063 A/pulse. By adjusting the number of pulses, the samples with desired carbon thicknesses were prepared. Further, in sample CM3a/4SiN12C, the SiNₓ interlayer (0.4 nm) was deposited by pulsed DC reactive sputtering.

**Characterizations.** The thicknesses of the OCs, in cross-section geometry, were measured by high resolution TEM (Philips CM300 FEG). The samples for TEM imaging were prepared in various steps. ARXPS measurements (VG ESCALAB 2201-XL) were performed in an ultrahigh vacuum (~10⁻¹¹ Torr) with varying TOA from 15 to 65 °C. The monochromatic Al Kα was used as the X-ray source (1486.6 eV). The micro-Raman measurements were performed with a Jobin Yvon LABRAM-HR setup. The excitation wavelength of 488 nm from an Ar laser was used for visible Raman measurements while an excitation wavelength of 632.8 nm from an He-Cd laser was used for UV Raman measurements. The spot size was fixed at ~1 μm for the analysis.

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