Boosting contact sliding and wear protection via atomic intermixing and tailoring of nanoscale interfaces

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Friction and wear cause energy wastage and system failure. Usually, thicker overcoats serve to combat such tribological concerns, but in many contact sliding systems, their large thickness hinders active components of the systems, degrades functionality, and constitutes a major barrier for technological developments. While sub-10-nm overcoats are of key interest, traditional overcoats suffer from rapid wear and degradation at this thickness regime. Using an enhanced atomic intermixing approach, we develop a ~7- to 8-nm-thick carbon/silicon nitride (C/SiNx) multilayer overcoat demonstrating extremely high wear resistance and low friction at all tribological length scales, yielding ~2 to 10 times better macroscale wear durability than previously reported thicker (~20 to 100 nm) overcoats on tape drive heads. We report the discovery of many fundamental parameters that govern contact sliding and reveal how tuning atomic intermixing at interfaces and varying carbon and SiN, thicknesses strongly affect friction and wear, which are crucial for advancing numerous technologies.

INTRODUCTION

Wear and friction remain the two most critical and long-standing issues in moving mechanical systems/devices (MMSDs) at all length scales (1–3). High friction is undesirable because of the extra mechanical energy that has to be consumed to overcome it, leading to energy losses. It is estimated that about one-third of automobile fuel is used just to overcome the unwanted effects of high friction (1, 2). This excessive use of fuels and energy wastage is deleterious toward the environment and human health and incurs huge economical losses in the long term. At the same time, material wear is also a critical concern because the rapid removal and degradation of material result in early failure of various systems/devices (1–3). Magnetic storage devices, such as read/write heads, recording media of tape drives (TDs) and hard disk drives, probes for atomic force microscopy (AFM), micro- and nano-electromechanical systems (MEMS and NEMS), and many engineering scale components are some examples of MMSDs that suffer immensely from the adverse effects of wear and friction (1–19). In general, from environmental, human health, and economical viewpoints, even a small fraction of friction and wear reduction is vital for energy savings and increasing the operational lifetime of systems.

Surface coatings have evolved over the years as an excellent route to modify friction and wear (2, 4–9). With miniaturization and advancement of modern devices/systems, the thickness budget of surface coatings in many devices and systems is shrinking year by year (4–6, 8–15). However, most of the commonly used overcoats are very thick (from a few tens to hundreds of nanometers) (1, 13–19), provide insufficient wear durability in many rigorous tribological conditions (13–19), and hinder the intrinsic functionality of several practical systems and devices (4–6). For example, Erdemir et al. (1) used a ~600-nm-thick overcoat to minimize friction and wear. Among the widely used overcoats, namely, silicon nitride (SiNx), chromium oxide (CrOx), chromium nitride (CrNx), amorphous carbon (a-C), zirconium oxides (ZrO2 and Zr2O3), and their various combinations, most of them suffer from excessive wear and friction despite being quite thick (10–19). Wear and friction issues are particularly critical for TDs owing to their contact recording architecture, where the recording head is always kept in contact with the tape media that slides across the head (9, 12–17). As a consequence, the tape head experiences severe wear and, over time, induces a large pole tip recession, leading to an increased magnetic spacing, degradation of recording functionality, and, subsequently, early failure of the TD (12–17). Most ~20- to 100-nm-thick coatings showed poor wear resistance and/or survived less than ~1.7 to 5 million meters (Mm) of tape sliding in tape head wear (THW) tests, with a-C films grown by energetic processes demonstrating relatively better wear resistance (12–19). Hence, improving the wear resistance of overcoats at reduced thicknesses is one of the most fundamental requirements to increase the storage capacities and operational lifetime of TDs (9, 17).

In general, the development of a single sub-10-nm-thick overcoat to largely modify friction and wear in the nano-, micro-, and macroscales is of huge interest for many current and future applications such as TDs, MEMS/NEMS, AFM tips, and other common tribological applications. However, doing so continues to be challenging as the structural, tribological, and protective characteristics of these overcoats diminish notably at sub-10-nm thicknesses (4, 8, 12, 18–24). Here, we propose a novel method of atomic intermixing and precise tailoring of the nanoscale interfaces in ~7- to 8-nm-thick C/SiNx multilayer overcoats via depositing C and SiNx layers alternately and using a high-energy carbon treatment to largely control wear and friction at all tribological length scales. By extensive optimization, we develop a new type of overcoat comprising...
two consecutive cycles of 0.7-nm SiNₓ/high-energy carbon treatment/2.75-nm carbon (90 eV) (sample M, Fig. 1A), yielding super-high wear resistance and low-friction characteristics at the nano- and microscale on a flat Al₂O₃ + TiC (AITIC) composite ceramic substrate, as well as high macroscale wear durability on a tape head, despite being only ~7 to 8 nm in thickness.

RESULTS AND DISCUSSION

Atomic intermixing and tailoring of nanoscale interfaces

Since carbon has strong affinity with both silicon and nitrogen, we hypothesized that the creation of robust interfaces, atomic intermixing, and tailoring of nanoscale interfaces can be performed by the deposition of ultrathin SiNₓ and carbon layers alternately while varying their thicknesses and tuning the energetics of the arriving carbon atoms/ions. We executed our experiments in view of this proposed concept and deposited alternating SiNₓ layers (thicknesses of ~0.7 to 1.5 nm) and carbon layers (thicknesses of ~2 to 2.75 nm at 4 and 90 eV) for 2 cycles, without and with high-energy carbon treatment (Tₙ) at 350 eV (Fig. 1A) (see Supplementary Discussions 1 and 2). Here, 4 eV is the energy of sputter-processed carbon, while 90 and 350 eV are the energies of carbon processed by a filtered cathodic vacuum arc (FCVA) (4, 25). The thickness of the overcoat is a critical parameter to us because the development of many technologies is directly linked to the reduction of the overcoat thickness. The intended thickness of these overcoats is kept to ~7 to 8 nm, which is in the ultrathin regime. Hence, even a modest alteration of overcoat thickness in this regime can cause a big change in the percentage scale, unlike overcoats with hundreds of nanometers in thickness. Therefore, we used high-resolution transmission electron microscopy (HRTEM) to directly and accurately measure the thickness of these overcoats grown on Si substrates. Fig. 1B shows the HRTEM images of a few selected samples (see Supplementary Discussion 3 for additional details and HRTEM images of all samples). We applied capping layers of tantalum before and after the overcoats are deposited on the Si substrates specifically for the HRTEM cross-sectional imaging measurements. This was done because the lighter contrasts of both carbon and SiNₓ are similar to the native...
SiO$_x$ layer on Si and the epoxy layer used to glue the sample during sample preparation. On the other hand, tantalum as a capping layer shows darker contrast in HRTEM. Thus, the cross-sectional HRTEM samples with the tantalum capping layers assist in accurately determining the thickness of the overcoat by eliminating the regions of epoxy and SiO$_x$. Therefore, in all the samples, the overcoat thickness can be measured between the two capping layers (Fig. 1B). The total thicknesses of these composite nanoscale multilayer structures were measured to be ~7 to 8 nm, which were in agreement with the expected thicknesses.

The general picture of atomic mixing and the creation and tailoring of nanoscale interfaces were first visualized theoretically by performing Monte Carlo–based transport and range of ions in matter (TRIM) calculations (26). We observed that the volume of interaction significantly increases with increasing the energy of the carbon ions/atoms arriving at the substrate and with the reduction of the SiN$_x$ layer thickness, resulting in an enhanced distribution of carbon in the interlayer and substrate regions as well as increased recoiling of the interlayer and substrate atoms (see fig. S2A). Next, we simulated the atomic distributions for the actual experimental overcoat designs (Fig. 2, panels 1 to 4). The 4-eV carbon in samples F and K induced a minimal volume of interaction that was limited to the surface of the SiN$_x$ layers. No recoiled atoms from any layer or substrate were observed. In contrast, the application of 90-eV carbon in samples G, I, J, and L led to a much higher volume of interaction with the observation of recoiled atoms from the intermediate layers and the substrate. However, when 350-eV carbon ions were introduced for a short span of time (see Fig. 1 caption) in combination with 90-eV carbon ions in samples H, M, and E, the volume of interaction and number of recoiled atoms were markedly increased (see Supplementary Discussion 4 for the comprehensive TRIM calculations). Thus, FCVA-processed carbon allows extensive atomic intermixing and the creation of relatively more mixed interfaces than its sputtered counterpart.

Next, we used x-ray photoelectron spectroscopy (XPS) (Fig. 3) and Auger electron spectroscopy (AES) depth profiles (graphs shown in section “Engineering and controlling the wear on commercial TD heads”) to qualitatively probe the intrinsic structure and composition of the overcoats and, in doing so, gain an insight into the interface tailoring and atomic mixing. The AES depth profiles revealed the presence of C, Si, and N in the overcoat region as evident from their higher intensities up to the overcoat/substrate interface region. Beyond the overcoat/substrate interface region toward greater sputter times (depths), the intensities of O, Al, and Ti started to increase and eventually reached a saturated level, which is in agreement with the expected composition of the AlTiC substrate. In the overcoat region, the variation of the elemental compositions of C, Si, and N with sputter time (or depth) appeared to be consistent with the expected layered composition of the overcoat. The AES depth profiles show that there is one interface (I) at the film/substrate boundary for monolithic overcoats (samples B and C) and four interfaces at each boundary for all C/SiN$_x$ multilayer structures, i.e., C/I$_1$/SiN$_x$/I$_2$/C/I$_3$/SiN$_x$/I$_4$/substrate, which are in agreement with the prepared C/SiN$_x$ multilayer designs. Each interface region was observed to be highly mixed (i.e., interfaces are not abrupt) as a result of atomic intermixing.

Furthermore, we recorded various high-resolution XPS spectra at different depth levels and thoroughly examined all the XPS results (see Supplementary Discussions 5 and 6). We present the results of the deconvoluted high-resolution XPS spectra of C 1s, Si 2p, N 1s, Ti 2p, and Al 2p for C/SiN$_x$ multilayer samples G, L, and M (Fig. 3, A to F). From figs. S3 (before deconvolution) and S4 (A to I) (after deconvolution), we noticed that the signals related to the substrate atoms (Al 2p and Ti 2p peaks, as well as the Ti-C peak in the C 1s spectra) were negligible when the XPS spectra were recorded without performing a depth profile (0 s), because of the limited photoelectron escape depth. Therefore, high-resolution spectra were recorded at different depth levels to examine the chemical bonds present at the film/substrate (FS) interface. A comprehensive analysis of chemical and interfacial bonding as a function of different etching times for samples G, L, and M (fig. S4, A to I), together with chemical bonding analyses of additional samples H and K (fig. S4I), can be found in Supplementary Discussion 6. Since the XPS photoelectron escape depth was large enough to examine the top C/SiN$_x$ layers (mainly the top two to three layers), the chemical bonds based on C/Si/N atoms can be visualized even without depth profiling. On the basis of the signal for Ti–C bonding (arising from the AlTiC substrate) in the C 1s spectra, the etching times required to reach the FS interfaces and substrate regions were determined, which varied from sample to sample (i.e., 100 s for sample G, 125 s for sample L, and 150 s for sample M). Here, in Fig. 3 (A to F), we present the deconvoluted XPS spectra of samples G, L, and M that were measured as-received before etching (0 s), as well as after their respective etching times to reach the FS interface. Except Ti–C peak, the C 1s spectra recorded without performing a depth profile (0 s) showed Si–C, sp$^2$C, sp$^3$C, C–O, and C=O bonding peaks for all the C/SiN$_x$ multilayer samples. However, the C 1s spectra recorded after etching time of 100 s for sample G, 125 s for sample L, and 150 s for sample M showed Ti–C peak, in addition to other peaks, as the substrate is approached. Other types of bonding are evident from the Si 2p, N 1s, Ti 2p, and Al 2p spectra. The Al–O and Ti–C peaks correspond to the AlTiC substrate, whereas Si–N is assigned to the SiN$_x$ layers. Various carbon–carbon and carbon–oxygen bonds reveal the tuning of carbon chemistry and carbon hybridization. New hybrid interfacial bonds, namely, Si–C, Si–O/Si–O–N, (Al, Ti)N, sp$^2$C–N/Nitrile/Si–O–N, sp$^3$C–N, (Ti, Al)/N/Ti–C–O–Al–N, (Ti, Al)N–O, and Al–N were created. Thus, apart from the intrinsic bonds present in the layer/substrate material, we achieved the creation of several new hybrid interfacial bonds as a consequence of interfacial chemical interactions between different layers, as well as between the layer(s) and the substrate. FCVA-processed C/SiN$_x$ multilayer structures yielded more interfacial bonding than sputter-processed C/SiN$_x$ multilayer structures due to the use of higher carbon energies, which corroborates with the TRIM calculations. As an example, to compare the interfacial bonding between FCVA-processed and sputter-based C/SiN$_x$ multilayer overcoats with similar carbon thickness (2.75 nm in each layer) and SiN$_x$ thickness (0.75 nm in each layer), we estimated the amount of interfacial Si–C bonding from the Si 2p spectra for sample K (sputtered C/SiN$_x$ multilayer overcoat) and sample L (FCVA-processed C/SiN$_x$ multilayer overcoat). The bonding fraction of Si–C bonds was estimated to be 18.6% in sample K, which was markedly increased to 45.5% in sample L, confirming that the FCVA-processed C/SiN$_x$ multilayer overcoats tend to form a greater amount of interfacial bonds. Since sp$^3$ bonding is an important structural parameter that influences the functional properties of amorphous carbon films (24, 25, 27–30), we measured sp$^3$ bonding using Raman spectroscopy based on the movement of the G peak under ultraviolet excitation.
following the three-stage model (25, 28) and also by deconvolution of the high-resolution XPS C 1s spectra (28, 31) (Fig. 3G; see Supplementary Discussion 7 for a detailed discussion). Spectroscopic analyses showed that FCVA-processed monolithic carbon and C/SiNx multilayer structures have carbon microstructures containing much higher sp³ carbon bonding and less ring-like sp² carbon networks than their sputtered counterparts. For example, when comparing C/SiNx multilayer samples K and L, while both samples have similar carbon thickness (2.75 nm in each layer) and SiNₓ thickness (0.75 nm in each layer) stack, the sp³ bonding is about three times higher (~59%) in sample L than in sample K (~21.5%). This is because the energetics of carbon in FCVA (90 eV) facilitate subsurface growth and hence subplantation (28, 31), resulting in higher sp³ bonding than sputtered carbon (<5 eV). Among the FCVA-processed C/SiNₓ multilayer overcoats, the sp³ bonding was observed to increase with increasing 90-eV carbon layer thickness from 2 nm per carbon layer (samples G and H) to 2.75 nm per carbon layer (samples L and M). Ball-and-stick chemical models (Fig. 3H) were also prepared on the basis of the Raman results, showing higher sp³ bonding and negligible ring-like sp² carbon network for FCVA-processed carbons (samples C and E) and vice versa for sputter-deposited carbon (sample B). Thus, the increased overcoat robustness due to increased interfacial strength between the layers in the overcoat, enhanced FS robustness, improved adhesion of overcoat with substrate, and tuning of the carbon microstructure (high sp³ versus low sp²) are expected to have a substantial influence on the overcoat’s resistance to contact sliding at the nano-, micro-, and macroscales.

Nanoscale surface, mechanical, and tribological properties

The root-mean-square surface roughness (Rq) of bare and coated AlTiC, measured using AFM, is shown in Fig. 4A. The Rq of uncoated AlTiC was measured to be ~8 nm. In comparison, the overcoated AlTiC samples also showed an Rq of ~6 to 8 nm. Since amorphous carbon is an intrinsically smooth material (20, 21), the origin of the large Rq for these coated samples is mainly due to the pronounced influence of the AlTiC substrate roughness. This is evident when comparing the roughness of auxiliary C/SiNₓ bilayer overcoats deposited on both rougher AlTiC and smoother Si wafer substrates, whereby a much lower Rq (~0.1 to 0.2 nm) was obtained for the overcoats on Si (see Supplementary Discussion 8). Thus, the carbon-based overcoats are intrinsically smooth. The roughness profiles of uncoated AlTiC and AlTiC coated with a few selected overcoats are presented in Supplementary Discussion 8.
Fig. 3. Interfacial and structural properties. Deconvolution of various XPS core level spectra recorded without performing a depth profile (0 s) and after an etching time of 100 s for sample G, 125 s for sample L, and 150 s for sample M. (A) Deconvolution of C 1s spectra for sample G (0 and 100 s), sample L (0 and 125 s), and sample M (0 and 150 s). (B) Deconvolution of Si 2p spectra for sample G (0 and 100 s), sample L (0 and 125 s), and sample M (0 and 150 s). (C) Deconvolution of N 1s spectra for sample G (0 and 100 s), sample L (0 and 125 s), and sample M (0 and 150 s). (D) Deconvolution of Ti 2p spectra for sample G (100 s), sample L (125 s), and sample M (150 s). (E) Deconvolution of Al 2p spectra for sample G (100 s), sample L (125 s), and sample M (150 s). (F) Different peaks corresponding to the different chemical bonding species. (G) Variation of sp3C bonding based on Raman and XPS analyses. The three-stage model, proposed by Ferrari and Robertson (25), was used to estimate sp3 bonding by Raman spectroscopy. (H) Ball-and-stick chemical models for samples B, C, and E. Lime, gray, and red color balls correspond to sp2-carbon, sp3-carbon, and oxygen atoms, respectively.
Fig. 4. Surface, mechanical, and tribological properties. (A) (i) $R_q$ and nanoscale friction, (ii) hardness and elastic modulus, and (iii) CNP and CNF for various samples. (B) (i) Schematic of the experimental setup for ball-on-disk tribological tests. (ii to ix) Ball-on-disk microscale tribology showing the frictional curves and COF values for different samples. One cycle corresponds to a distance of 1.257 cm. All the experimental conditions were kept the same to limit any external influence on microscale tribology (see Materials and Methods and Supplementary Discussion 2). The nanoscale COF was found to be similar in these samples, although closer inspection revealed that it was marginally higher in the carbon superlattice overcoat (sample E) and C/SiN$_x$ multilayer overcoats than in the monolithic carbon overcoats (samples B and C). Furthermore, in a microscale friction test environment, sample M exhibited the lowest and most stable friction.
Next, we examined the nanomechanical properties [hardness (H) and elastic modulus (E)] and nanotribological properties [nanoscale coefficient of friction (COF) and nanoscratch resistance] of these samples (Fig. 4A). AFM topography images were recorded from various locations before and after nanoindentation and nanoscratch tests to visualize the indent/scratch marks (see Supplementary Discussion 9). Although the measured mechanical properties show a significant substrate influence due to the extremely low thickness of the overcoats, we observed that the H and E values were higher for the FCVA-processed carbon-based samples than that for the sputter-coated counterparts due to the presence of higher sp^3 carbon bonding in the former. Furthermore, all these samples, including bare AlTiC, showed very low and similar nanoscale friction (COF < 0.2), indicating that carbon microstructure and interface chemistry do not have much influence on the nanoscale friction. To assess the nanoscale scratch resistance, we measured the average critical normal force (CNF) and critical normal displacement (CNP) (9). The CNP and CNF are measured at the onset of critical events, with higher values corresponding to a better scratch resistance (9). Carbon superlattice sample E and the C/SiNx multilayer samples with higher SiN_x thickness revealed better nanoscratch resistance than the monolithic carbon overcoats. The reduction of SiN_x thickness decreased the nanoscratch resistance (as seen in samples K and L), but the application of high-energy carbon treatment in conjunction with lower (higher) SiN_x (carbon) thickness gave the highest nanoscratch resistance (sample M). We demonstrate a crucial finding here that the increased interfacial strength/adhesion is the key parameter for obtaining excellent nanoscratch resistance, followed by the availability of higher sp^3 carbon bonding.

Controlling and engineering microscale wear and friction

We performed microscale ball-on-disk tribological measurements to understand how the creation of multiple interfaces and associated atomic intermixing and tailoring of nanoscale interfaces control the friction and wear of carbon-based overcoats (Figs. 4B and 5A). The friction of the sample is judged on the basis of the COF and stability of the frictional curves where a lower value of COF and higher stability (or less fluctuations) of the frictional curves signify a better overcoat. A better wear resistance correlates with a faint wear track on sample surface and less debris transfer to the ball. Bare AlTiC gave a fluctuating frictional curve with a high COF (>0.4), which was reduced by ~27 and ~67% after the application of monolithic carbon in samples B and C, respectively. Bare AlTiC also showed significant wear that was reduced in sample B and was barely visible in sample C. This suggested that overcoats are necessarily required to mitigate friction and wear. In contrast, monolithic SiN_x showed the highest COF (~0.65) with continuous fluctuations throughout the measurement and resulted in extremely high wear. Overall, monolithic carbon deposited at moderate energy (90 eV) by FCVA demonstrated the lowest wear and friction of all the monolithic overcoats.

Next, we classified the carbon superlattice and C/SiNx multilayer samples into three types to present and explain their microscale tribological behavior. In type I, samples E, F, G, and H are included, which contain ~2-nm-thick carbon layers in the lower and upper sides of the multilayer/superlattice stacks. Carbon superlattice sample E showed very low COF (~0.14) and a stable frictional curve with high wear resistance. In contrast, the C/SiNx multilayer structures in designs F and G demonstrated significantly higher and fluctuating friction with very severe wear, which is totally opposite to what was observed with their nanoscale friction and nanoscratch tests, thus displaying two mutually conflicting behaviors (see Figs. 4, A and B, and 5A). However, when the C/SiNx multilayer overcoat design was slightly tailored in sample H, it yielded significantly reduced microscale friction and wear. This prompted us to prepare and test several auxiliary C/SiNx bilayer overcoats (Fig. 4B,v, vi, vii, and ix) with varied layer thicknesses of SiN_x and carbon, and with varied T_n, to produce more effective overcoat designs. The results for the auxiliary C/SiNx bilayer samples suggest that, for effective tribological coatings, the carbon thickness should be close to 3 nm, SiN_x thickness needs to be low, and high-energy carbon treatment should be performed (see Supplementary Discussion 10 for details).

Taking the knowledge obtained from the tribological analysis of auxiliary samples, we move to type II samples I and J, which have thicker carbon (~2.75 nm) and thinner SiN_x (~0.75 nm) on either the lower or the upper side of the C/SiNx multilayer stacks. The tribological results are consistent with the conclusions drawn from the auxiliary sample analysis, as samples I and J demonstrated significantly lower friction and wear than sample G, with sample J slightly outperforming sample I. These results inspired the design of type III samples, which include samples K, L, and M that have 0.7- to 0.75-nm-thick SiN_x and 2.75-nm-thick carbon layers for both of the lower and upper sides of the multilayer stacks. These type III samples eventually showed further reduction of friction and wear. Sample K yielded ~68 and ~36% lower friction than samples F and B, respectively. Similarly, sample L yielded ~69% lower friction than sample G. Among all overcoats, type III sample M yielded the best microscale tribological performance in terms of very low and stable friction (COF, ~0.14) and super-high wear resistance. Earlier, it was noted that sample M also outperformed all samples in nanoscale friction and nanoscratch test environments. This shows that a multilayer stack with thinner SiN_x (~0.7 nm) and thicker carbon (~2.75 nm) deposited at a carbon ion energy of 90 eV with a high-energy (350 eV) carbon treatment, such as T_n, is pivotal for obtaining extraordinary friction and wear properties on both the micro- and nanoscale.

We repeated the microscale tribological tests many times for the reproducibility of the results (see Supplementary Discussion 10) and examined the wear tracks by Raman spectroscopy to uncover the underlying mechanisms. We present the wear track analyses of a few selected samples by Raman spectroscopy in Fig. 5B. Among the sputter-processed C/SiNx multilayer overcoats, sample K showed relatively less structural damage and wear of carbon than sample F, as defined by comparing the shapes of the spectra outside and on the wear track. Similarly, among the FCVA-processed C/SiNx multilayer overcoats, sample J showed relatively less structural damage and wear of carbon than sample G. In general, the Raman results showed significant damage and removal of carbon for the overcoats whose wear tracks were found to be most severe in the optical microscope images (see Supplementary Discussion 11 for detailed Raman analysis). In addition, some degree of wear-induced sp^3 → sp^2 bonding transformation was also observed in these overcoats.

Engineering and controlling the wear on commercial TD heads

These ~7- to 8-nm-thick overcoats were applied onto TD heads to test their wear resistance in a rigorous macroscale THW test environment. The THW tests closely mimic the operation of actual TDs where overcoated heads are exposed to magnetic tape sliding for a long period of time (~12) (Fig. 6A; see Supplementary Discussion 12).
Fig. 5. Wear analysis after microscale ball-on-disk tribological tests. (A) Optical images of the balls (rows 1 and 3) and sample surfaces (rows 2 and 4) after the tribological measurements. The images reveal the amount of debris transferred to the balls and the severity of the wear tracks formed on the sample surfaces. Scale bars, 100 μm. Bare AlTiC showed significant wear, whereas sample M yielded the least wear. (B) Raman spectra of selected samples recorded from outside the wear track and at various locations (Loc) on the wear track to examine the wear in relation to the overcoat design. The sputter-processed C/SiN_x multilayer in sample F experienced significant wear, indicating a considerable amount of overcoat removal and damage to the carbon layers, as visualized by the noisy Raman spectra on the wear tracks when compared to outside of the wear track. However, the wear was minimized in sample K because of the tailoring of the carbon and SiN_x thicknesses, resulting in a small amount of carbon removal and minor structural damage to the carbon layers, although a D peak emerged when Raman spectra were recorded from the wear tracks, suggesting a higher amount of disordered sp^2 carbon. A similar behavior to the sputter-processed overcoats was observed for the FCVA-processed C/SiN_x multilayers, where sample G showed higher wear, but the wear was minimized by tuning the carbon and SiN_x thicknesses in sample J (see Supplementary Discussion 11 for a detailed wear track analysis by Raman spectroscopy).
These tests were performed up to a tape sliding distance of 5 Mm. After 5 Mm of THW testing, most of the overcoats were completely worn off except samples C, E, and M (see Supplementary Discussion 12 for detailed analyses). Optical microscope images of the heads with the three best-performing overcoats before the THW test (0 Mm) and after test durations of 1, 2, and 5 Mm of THW from the same location of each sample are shown in Fig. 6B. The images reveal the tape head architecture: the AlTiC substrate and closure, an Al2O3 dielectric gap (middle dark gray strip extending in the horizontal direction), and the magnetic read/write poles and shields in the Al2O3 gap region. We observed, in general, that as the tape test progressed, the overcoat experienced increasing wear with THW test duration. Monolithic FCVA-processed carbon (sample C) experienced significant wear near the AlTiC substrate/closure edges, as shown by discoloration in the optical images and pointed out in Fig. 6B. On the contrary, the C/SiNx multilayer overcoat in sample M and carbon superlattice sample E demonstrated extraordinary wear resistance, as most of the coating in each case was still present on the entire area of the head after the THW test.

We used AES imaging and AES depth profiling to obtain a greater insight into the wear durabilities of the overcoated heads. We present here the AES images (Fig. 6C) and AES depth profiles (Fig. 7) for four selected samples C, E, G, and M, while the complete AES analysis with AES images and depth profiles of eight samples (namely, samples C, E, F, G, H, K, L, and M) can be found in Supplementary Discussion 12. In the AES images, the elements C, O, Al, and Si were mapped. AES images revealed that, apart from samples C, E, and M, all the other overcoats were completely removed.

Fig. 6. Long-term THW test and wear analysis. (A) Schematic of the THW test setup used in the present work comprising tape supply/take-up reel components, tape guides, and the tape head to be tested, which was kept in contact with the sliding tape media at a constant tension. This simulates the operation of actual TDs. Since most of the previous thicker (~20 to 100 nm) overcoats could survive up to a maximum of 1.7 to 5 Mm of tape sliding in the THW test, we performed THW tests up to a tape sliding distance of 5 Mm to analyze the wear of our ~7- to 8-nm overcoats. (B) Optical microscope images of selected tape heads after THW tests. The brighter and darker portions indicate the presence and removal of overcoats, respectively. Although sample G demonstrated good wear resistance, it yielded very severe wear near the AlTiC substrate/closure edges adjacent to the Al2O3 gap region and inside the gap. In contrast, the wear was found to be minimal in samples E and M, suggesting higher wear resistance. (C) AES images to assess wear based on elemental mapping of C, O, Si, and Al. Before AES imaging, SEM images were recorded. The wear was evaluated on the basis of the intensities of C (from the overcoat) and Al/O (from the substrate), where a warmer/brighter color represents higher intensities and cooler/darker color represents lower intensities, according to the color scale bar. The C/SiNx overcoat in sample M demonstrated the best wear resistance.
after 5 Mm of THW testing, corroborating well with the optical images. Moreover, apart from carbon superlattice sample E and C/SiNx multilayer sample M, all the other overcoated heads experienced a significant amount of charging in the gap region during scanning electron microscopy (SEM) imaging. Only samples E and M had overcoats that were still covering the entire Al2O3 gap region and the adjacent AlTiC substrate/closure edges and exhibited uniform wear across the head. While monolithic carbon sample C showed good protection at most locations on the AlTiC, it experienced very nonuniform wear that was most significant at the AlTiC substrate/closure edges and Al2O3 gap region. Since the magnetic read/write poles and shields are contained here, this region is of interest for wear protection. AES depth profiles (Fig. 7) after 5 Mm of THW tests also confirmed that most of the overcoats had been completely worn off except samples C, E, and M. We calculated that about 65, 48, and 62% of the coating remained on the heads for samples C, E, and M, respectively, after the THW tests. Although the amount of coating removed for samples C and M was similar, the locations selected for depth profile analyses were further away from the Al2O3 gap and AlTiC substrate/closure edges where sample C showed poorer wear durability. What is interesting here is that sample M showed excellent wear resistance both at the AlTiC substrate/closure edges and Al2O3 gap, as well as at the location where the depth profile was performed, which is further away from the area of interest. Thus, on the basis of the wear analyses by optical images, AES maps, and AES depth profiles, we conclude that the C/SiNx multilayer overcoat design in sample M is the best performing in terms of tape sliding wear durability, followed by the overcoat designs in samples E and C. While studying the wear durability of a 50-nm-thick Cr2O3 overcoat, Shi et al. (17) reported that a significant thickness of the overcoat (7 nm) was removed after just 1 Mm of tape wear. In comparison, our overcoats with just 7 to 8 nm in thickness (samples C, E, and M), and especially sample M, have shown without a doubt to have much higher wear durability than the Cr2O3 overcoat. In general, despite being thinner, these three overcoats also fared better in terms of wear durability than thicker overcoats (~20 to 100 nm) (13–19).

**Deterministic parameters and mechanisms for friction and wear**

Conventionally, sp3 bonding is the key parameter that governs wear resistance, while both sp3/sp2 bonding and surface chemistry/surface passivation control the friction characteristics of amorphous carbon films (4, 6, 29–33). We uncover here many other novel critical parameters which govern the friction and wear behavior at the sub-10-nm thickness regime on all tribological scales. The interface robustness (both within the overcoat and at the overcoat/substrate boundary), increased adhesion, and possession of a critical carbon thickness are found to be the major parameters needed to control and engineer the wear and friction of amorphous carbon–based ultrathin overcoats at all length scales. We also discover that interfacial robustness and critical carbon thickness are mutually interdependent.

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**Fig. 7. AES depth profiling to examine overcoat wear after long-term THW tests.** After 5 Mm of THW tests, AES depth profiles were performed at selected locations on the head as highlighted by the red dot in each SEM image of Fig. 6C. The corresponding AES depth profile from an unworn region outside of the area of magnetic tape/ head interaction for each sample was taken as a reference for comparison purposes. The depth profiles of samples C, E, G, and M are shown here, while those of samples F, H, K, and L are presented in fig. S10D. AES depth profiles for C/SiNx multilayer structures reveal the fluctuation of C, Si, and N intensities when moving away from the surface, approaching/crossing the C/SiNx interfaces, and reaching the film/substrate boundary, corroborating well with the actual designs of these multilayer structures. The immediate drop in C intensity and the immediate increase in O intensity in the first 50 s of most of the depth profiles after 5-Mm THW tests indicate that most of the head overcoats had been completely worn off, except in samples C, E, and M. Sample M with just a 7- to 8-nm-thick overcoat displayed the best wear resistance (about 62% overcoat is still present after 5 Mm of THW) out of all the overcoats used in the present work and even surpasses the wear resistance of previously reported thicker and sputter-deposited ~20- to 100-nm coatings of CrNx, CrOx, CNx, c-BN, yttrium-stabilized ZrO2, W–CH, a–CH, Al2O3, and TiN (13–16).
parameters that need to be tailored according to the scale of tribological measurements. In general, ~2-nm and ~2.5- to 2.75-nm carbon thicknesses (in each layer) and adequate interfacial robustness (based on 4- or 90-eV carbon) are sufficient at the nano- and microscale, respectively, to achieve excellent wear resistance and low friction with C/SiNₓ multilayer overcoats. Similarly, ~2.75- to 3-nm carbon thickness and significantly high interfacial robustness/adhesion (based on 350-eV carbon) are required to withstand the wear conditions in a macroscale tribological environment. We elaborate on this here.

The creation of multiple nanoscale interfaces and the tuning of the energy of the arriving carbon ions/atoms in C/SiNₓ multilayer designs have led to enhanced atomic intermixing (formation of nanocomposite interfaces) and interfacial bonding, which increased the interfacial strength/robustness between the overcoat and the substrate, thereby contributing to improved adhesion, and also increased the robustness of the overcoat itself. Similarly, the use of high-energy carbon T₁ in carbon superlattice sample E promoted greater atomic mixing and further contributed to the increased adhesion of the overcoat with the substrate. This explains why the carbon superlattice and C/SiNₓ multilayer overcoats in certain designs, for example, in samples E, F, G, and M, showed much better nanoscratch resistance than the monolithic carbon overcoats, with sample M being the best performing. Sample F, with a low amount of sp³ carbon (~2 nm in thickness), showed excellent nanoscratch resistance as well, indicating that increased interfacial robustness/adhesion driven by the introduction of relatively thicker (~1.5 nm) SiNₓ layers is the primary parameter for controlling scratch/wear resistance, followed by sp³ bonding at the nanoscale tribological environment (Fig. 4A). Samples F and G, both of which have ~2-nm carbon layers in multilayer stacks, showed excellent nanoscratch resistance, which suggests that even 2-nm carbon thickness is sufficient at nanoscale to obtain excellent tribological results due to the use of comparably lower measurement loads unlike at the micro- and macrotribological scales.

In the micro- and macroscale tribological environments, low friction can be achieved in both highly sp³- and highly sp²-bonded a-C films, thus explaining why samples B, C, and E showed low friction. The low friction in highly sp²-bonded a-C films (sample B) can primarily be attributed to water intercalation between the sp²-rich carbon layers and the low shear strength of sp² carbon. On the other hand, the low friction in samples C and E is attributed to the combined effects of regular surface passivation of carbon [in an environment with relative humidity (RH) of ~55%], a sufficient initial degree of sp² carbon bonding at the surface, and the tribo-induced transformation of sp³ → sp² bonding at the tribological interface during the test (4, 6, 29–33). The slight tribo-induced increase in sp² bonding was confirmed in our sp³-rich carbon-based films (see Supplementary Discussion 11). Since dangling bonds in carbon induce higher adhesion forces at the tribo interface, the regular passivation of dangling bonds by functional moieties such as C–H, C–OH, C–O, C=O, etc. (32) is achieved because of the regular supply of water vapor in a ~55% RH environment, and its continuous dissociation by contact stress and sliding contributes to the lowering of the COF or maintaining it at a constant level. Furthermore, the COF was more stable and lower in the FCVA-processed carbon films, which also yielded better wear resistance due to the presence of higher sp³ carbon bonding. Among the three samples B, C, and E, the relatively higher friction in monolithic sputtered carbon (sample B) can be attributed to the increased wear of the coating and eventual exposure of the underlying substrate surface to the counterface ball, which was confirmed by Raman spectroscopy analysis on the wear track.

The C/SiNₓ multilayer structures demonstrated mixed behaviors in friction and wear. Unlike their nanoscale scratch resistance, samples F and G exhibited the worst microscale tribological properties in terms of very high friction and severe wear. Here, the tribological effect of SiNx, which itself is a poor tribological material, dominated over the carbon microstructure (sp³/sp² bonding) and interfacial bonding, mainly because of an insufficient carbon thickness to withstand against the counterface at this scale. This was confirmed by the observation of improved tribological properties in both samples K and L where the carbon thickness was increased to 2.75 nm per layer (while the SiNₓ layer thickness was reduced accordingly). Moreover, adding high-energy carbon treatment led to the best microscale tribological properties in sample M due to increased atomic intermingling. Thus, we discovered that, for microscale tribology, carbon thickness plays a critical role in realizing superior tribological properties in C/SiNₓ multilayer systems. Upon reaching/crossing the critical thickness of carbon (~2.5 to 2.75 nm), the multiple nanoscale interfaces not only increase the robustness of the film-surface interface but also provide additional bonding strength within the film. These contribute to the improved abilities of overcoats to withstand high contact pressures (31, 34, 35) during sliding. This explains why the films with inferior interfacial robustness, such as sample B, do not easily survive the high loads applied by the counterface and are eventually worn off during the measurement. On the other hand, both low sp³-bonded (sample K) and high sp³-bonded (samples L and M) carbon-based overcoats showed higher wear resistance and lower friction than monolithic carbon; the interfacial robustness effect was found to be relatively more pronounced for carbon with higher sp³ bonding owing to its higher intrinsic strength. Furthermore, besides the aforementioned factors for low friction in these overcoats, the C/SiNₓ multilayer samples with high wear resistance could also contribute to low friction as a result of reduction of wear (4, 36), formation of nanocomposite interfaces due to extensive atomic mixing (C, Si, N, O, Al, and Ti) (1, 37, 38), and inclusion of Si/Si–O bonds (39, 40) in the carbon network.

When discussing the conditions for a harsh macroscale test environment (such as in THW tests), even the C/SiNₓ multilayer overcoat designs in samples K and L failed to provide good wear durability. The poor macroscale wear resistance in sample K is attributed to both the presence of low sp³ bonding and insufficient interfacial robustness. We recall that sample L with high sp³ bonding and engineered interfaces based on 90-eV carbon showed excellent tribological behavior in both nanoscale and microscale tribological environments. However, its poor wear resistance in the macroscale tribological environment of the THW test can be mainly attributed to insufficient interfacial robustness needed at this scale. Thus, while keeping the sp³ bonding and carbon thickness (based on 90-eV carbon) similar to that of sample L, when highly mixed interfaces were created by applying high-energy carbon treatment at 350 eV, which at the same time slightly increased the amount of carbon added to the overall stack, extraordinary macroscale wear durability was realized in sample M. This suggests that the combination of significantly higher interfacial robustness, sufficiently high sp³ bonding, and a suitable thickness of carbon (~2.75 to 3 nm) and SiNₓ are all critical and necessary parameters to obtain high wear durability/wear resistance in a rigorous macroscale tribological environment.
CONCLUSION

We have demonstrated how the degree of atomic intermixing and precise tailoring of nanoscale interfaces in ~7- to 8-nm-thick C/SiNx multilayer overcoat structures serve to influence their friction and wear engineering at all measurement scales. It was shown that wear and friction engineering of these ultrathin overcoats can be carried out by altering the thicknesses of the individual carbon and SiNx layers, performing high-energy carbon treatment, and tuning the carbon microstructure. We propose that high interfacial robustness, high adhesion of the overcoat, high sp³ bonding, and optimal carbon/SiNx thicknesses are critical parameters to realize high wear resistance and low friction with ultrathin overcoats. On the basis of extensive data, we also conclude that the preference of these critical parameters is highly dependent on the tribological scales: For nanoscale tribological tests, the adhesion of the overcoats (achieved by using a higher SiNx thickness of ~1.5 nm) is preferred over sp³ bonding in general, and a carbon thickness of ~2 nm in a C/SiNx multilayer is sufficient to attain good scratch resistance. In microscale tribological tests, sufficient carbon thickness (~2.5 to 2.75 nm) is a critical parameter, followed by adhesion and sp³ bonding. In macroscale tests, extremely high adhesion (based on a 350-eV carbon treatment), sufficient carbon thickness (~2.75 to 3.0 nm), and sufficiently high sp³ bonding are all equally important parameters to obtain high wear durability. The C/SiNx multilayer overcoat design of 2(0.7SiNx/TiC/2.75CF) (sample M), which comprised sufficient carbon thickness (~2.75 nm in each layer), lower SiNx thickness (~0.7 nm in each layer), and a high-energy (350 eV) carbon pre-treatment step, turned out to be the exceptional design that yielded excellent wear resistance/wear durability and low friction in tribological tests performed at all three tribological length scales: nano-, micro-, and macroscales. These important findings could aid the development of future ultrathin (<10 nm) overcoats having both super-high wear resistance and low friction that can be applied in advanced MMSDs at all length scales.

MATERIALS AND METHODS

Monolithic carbon, monolithic SiNx, carbon superlattice, and C/SiNx multilayer structures were deposited on plasma-cleaned flat AlTiC substrates, commercial magnetic tape head substrates, and flat Si substrates. Monolithic carbon and the carbon layers in the C/SiNx multilayer structures were deposited by either a low energetic process of pulsed direct current (dc) magnetron sputtering (AJA Inc.) or a high energetic process of FCVA (PVD75 system, which has both FCVA and magnetron sputtering capabilities; Kurt J. Lesker Company, USA), both situated in a class 10 K cleanroom. For all C/SiNx multilayer structures, the SiNx layers were deposited by magnetron sputtering in situ with carbon deposition. During the deposition of the FCVA-processed overcoats, the base pressure of the PVD75 system was kept at ~5 × 10⁻⁸ torr. The carbon films by FCVA were deposited at a C⁺ ion energy of 90 eV. In some samples, a high-energy carbon treatment (T1) was also performed at a C⁺ ion energy of 350 eV. The SiNx layers in these C/SiNx multilayer structures were deposited at a radio frequency (rf) power of 60 W and a working pressure of 3 mtorr. The deposition time was adjusted to tune the thicknesses of the SiNx and carbon layers. On the basis of the treatment time, four different types of high-energy carbon treatments, namely, T1, T2, T3, and T4, were performed. The times for T2, T3, and T4 were adjusted in such a way that they could contribute to <1-, <0.3-, and <0.5-nm thicknesses, respectively, to the total overcoat thickness. On the other hand, T1 was performed to intentionally get a thickness of 1.5 nm at 350 eV so as to construct the carbon superlattice sample E [2(T1/2CF)]. For the sputtered-processed overcoats, the mono-lithic carbon and carbon layers in the C/SiNx multilayer structures, as well as the SiNx layers, were deposited in the AJA system using computer-controlled magnetron sputtering. The base pressure was kept at ~7 × 10⁻⁹ torr during the deposition. The carbon films were deposited at a working pressure of 5 mtorr and an Ar flow rate of 20 sccm, while 100 W of dc power pulsed at a frequency of 150 kHz and a duty cycle of ~40% was supplied to the target. The SiNx layers in these C/SiNx multilayer structures were deposited at a working pressure of 3 mtorr and rf power of 120 W. The deposition time was adjusted to tune the thicknesses of the SiNx and carbon layers, respectively. A detailed discussion on the fabrication of these overcoats can be found in Supplemental Discussions 1 and 2 (28).

The overcoats deposited on flat AlTiC substrates were used for the characterization of interfacial, structural, and functional properties. The overcoats deposited on commercial tape heads were used for the THW tests. The overcoats deposited on Si substrates were used for thickness measurements by HRTEM (Philips CM200). Raman analyses were carried out using a Jobin Yvon LabRAM-HR setup. XPS spectra were recorded using a monochromatic Al Kα source (1486.6 eV) in a VG ESCALAB 220i-XL tool. AFM measurements were performed using a Bruker Innova setup to measure the surface roughness (Rq and Rd) of these overcoats. Nanoindentation measurements were carried out using a Hysitron TI 950 tool with a diamond Berkovich indenter, while nanotribological tests were performed in a Hysitron TI Premier setup to measure the nanomechanical properties (H and E), nanoscale COF, and nanoscratch resistance of the films. A quasi-static partial unload method was used to measure H and E as a function of indentation penetration depth (9). Given the ultralow thicknesses of these coatings, it was extremely difficult to avoid the substrate influence on the H and E values of the coatings. Therefore, we compared the H and E results extracted at a fixed penetration depth of ~7 to 8 nm for all samples, which normalizes the substrate influence for all coatings (9). Ramping force nanoscratch measurements were carried out to assess the overcoats’ scratch resistance through estimating CNF and CNP, indicating the onset of the first failure/delamination event. Microscale tribological measurements were carried out using a ball-on-disk nanotribometer (CSM Instruments) in a cleanroom booth (temperature of 23° ± 1°C and RH of 55 ± 5%), and a sapphire ball (Al2O3) with a diameter of 2.0 ± 0.1 mm was used as the counterpart. The initial mean and maximum Hertzian contact pressures for Al2O3-AlTiC contacts were estimated to be 0.32 and 0.48 GPa, respectively. AES imaging and depth profiles were recorded using a JEOL JAMP Auger Microprobe tool. Long-term THW tests were carried out up to 5 Mm in a custom-made tool to examine the wear durabilities of overcoated heads. It is important to mention that previous overcoats that have been applied onto the tape head, namely, CrN, CrO2, nitrogenated carbon (CNx), cubic boron nitride (c-BN), yttrium-stabilized ZrO2 (Y-ZrO2), hydrogenated amorphous carbon (a-C:H), tungsten incorporated C:H (W-C:H), diamond-like carbon (DLC), Al2O3, and titanium nitride (TiN), were very thick (~20 to 100 nm), and most of them suffered from early failure, although the a-C or DLC films fabricated by energetic processes yielded relatively better wear durabilities of all (12–19). During the tests, the overcoats deposited on LTO-5 tape heads were all tested against LTO-6 barium ferrite.
Fig. S8. Comprehensive friction and wear results for all samples.
Fig. S7.
Fig. S5. Structural properties.
Fig. S4. Interface analysis by XPS.
Fig. S3. XPS analysis.
Fig. S2H.
Fig. S2G.
Fig. S2C.
Fig. S2A.
Fig. S1. HRTEM imaging.

Supplementary Discussion 11. Wear track analysis by Raman spectroscopy.
Supplementary Discussion 10. Ball-on-disk microscale tribological results and analysis.
Supplementary Discussion 9. Nanomechanical and nanotribological properties results and analysis.
Supplementary Discussion 8. Surface roughness of the auxiliary samples.
Supplementary Discussion 7. Structural properties by XPS and Raman spectroscopy.
Supplementary Discussion 6. XPS results and analysis for chemical and interfacial bonding.
Supplementary Discussion 5. XPS spectra at various depths and consideration of various effects during analysis.
Supplementary Discussion 4. TRIM calculations results and analysis.
Supplementary Discussion 3. HRTEM results and analysis.
Supplementary Discussion 2. Sample preparation and characterization.
Supplementary Discussion 1. List of samples and their nomenclature.

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