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Ultra-thin a-SiN_x protective overcoats for hard disks and read/write heads*

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This paper reports that amorphous silicon nitride (a-SiN_x) overcoats were deposited at room temperature by microwave ECR plasma enhanced unbalanced magnetron sputtering. The 2 nm a-SiN_x overcoat has better anti-corrosion properties than that of reference a-CN_x overcoats (2–4.5 nm). The superior anti-corrosion performance is attributed to its stoichiometric bond structure, where 94.8% Si atoms form Si–N asymmetric stretching vibration bonds. The N/Si ratio is 1.33 as in the stoichiometry of Si_3N_4 and corresponds to the highest hardness of 25.0 GPa. The surface is atomically smooth with RMS < 0.2 nm. The ultra-thin a-SiN_x overcoats are promising for hard disks and read/write heads protective coatings.

Keywords: hard disk overcoat, ultra-thin, a-SiN_x, plasma enhanced magnetron sputtering
PACC: 6855, 6860, 8160B

1. Introduction

Rapid increases in the recording density of magnetic disks make it necessary to reduce the magnetic spacing between the magnetic disk and the read/write head. In order to increase the surface storage density to 1 Tb/in^2, the magnetic spacing must be reduced to 6.5 nm,[1−5] the thickness of the disk and read/write head overcoats would thus be about 2 nm accordingly, which typically consists of diamond-like carbon (DLC) or carbon nitride (CN_x).[1,2,5] Even with the current load–unload technology, the overcoats should provide some tribological protection. Most importantly the overcoats must provide the necessary barrier against corrosion and oxidation damage of the underlying magnetic layer and read/write heads.[3,4] In this case, deposition of an atomically smooth and dense ultra-thin coating with low defect density becomes crucial. However, a recent study has shown that the DLC and CN_x films cannot provide enough protective properties for magnetic disks and the read/write heads when the film thickness is decreased to 2 nm.[1,3,4]

Recently, amorphous silicon nitride (a-SiN_x) overcoats have become a new choice for magnetic disks and read/write heads' protective coating because of their high hardness, wear resistant, and protection against corrosion and oxidation, especially the upper coverage limit.[4] In our previous studies, we synthesized a-SiN_x films with stoichiometric structure, acceptable mechanical and corrosion properties, using microwave ECR plasma enhanced unbalanced-magnetron sputtering (MW-ECR PEUMS) technique.[6,7] In this paper, we report on properties and performances of ultra-thin a-SiN_x films with an emphasis on its surface roughness and protection against corrosion and oxidation. Pinhole-etch tests are carried out for 2 nm ultra-thin a-SiN_x films. The results show that our a-SiN_x films not only have a lower-coverage limit, but also significantly outperform the thicker reference films of a-CN_x,[3,4] which is now being applied in protective overcoats of commercial hard disk systems. This work becomes paramount for the ability to produce atomically smooth and pinhole-free a-SiN_x films over large areas for disk protective overcoats.

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2. Experiment

a-SiN_x films were prepared in the deposition chamber by our MW-ECR PEUMS system at room temperature. The base pressure of the chamber was below 2.5×10^{-3} Pa. Crystal silicon (purity 99.99%, 68 mm diameter disk) was used as the target material. A N_2-9% Ar mixture was chosen as the process gas, whose purity was 99.999%. During deposition, the total pressure was kept at 0.2 Pa, and the target power was fixed at 350 W radio frequency (RF). Silicon (100) wafers covered with 80 nm a-Al_2O_3 layers (a-Al_2O_3/Si multilayer structure) and silicon (100) wafers were used as substrates, the former for mimicking the structure of real read/write heads where the a-Al_2O_3 layer serves an insulation layer.[8] The substrate holder was connected with –100 V RF for accelerating Si^+ ions sputtered from target. We have detailed the deposition parameters in a previous publication.[6,7]

The precise thickness of films was measured by transmission electron microscope (TEM). Corrosion tests were carried out to evaluate the defect density of the films. In this test, 2 nm ultra-thin a-SiN_x films deposited on silicon wafers covered with an a-Al_2O_3 layer (a-SiN_x/a-Al_2O_3/Si multilayer structure) were immersed into an oxalic acid solution (0.1 mol/L $HOOCCOOH{\cdot}2H_2O$) for 24 h at room temperature. These corrosion conditions were much more rigorous than that used by the commercial read/write factory (0.05 mol/L, 4 min, 25 °C). The samples were then taken out of the solution, rinsed in de-ionized water, and dried with nitrogen. The corrosion damage was then examined by scanning electron microscope (SEM), and the number of spots counted and used as a measure of the corrosion protection performance of the overcoats. The film bonding structures were tested by x-ray photoelectron spectroscopy (XPS). The film hardness was obtained by nano-indentation. Surface morphology was measured by atomic force microscopy, where the root-mean-square roughness (RMSR) was obtained over sampling areas ranging to $1\times1\,\mu m^2$.

3. Result and discussion

3.1. Corrosion analysis

The anti-corrosion property is the most important characteristic of ultra-thin a-SiN_x films for disk and read/write head protective coatings. To measure the corrosion protection performance of a-SiN_x films for underlying layers, we prepared the a-SiN_x/a-Al_2O_3/Si multilayer structure samples. Figure 1 shows the cross-section TEM micrograph of such samples. As can be seen, a dense and atomically smooth a-SiN_x film was deposited on the a-Al_2O_3 layer. The precise thickness of the ultra-thin a-SiN_x film is 2 nm.

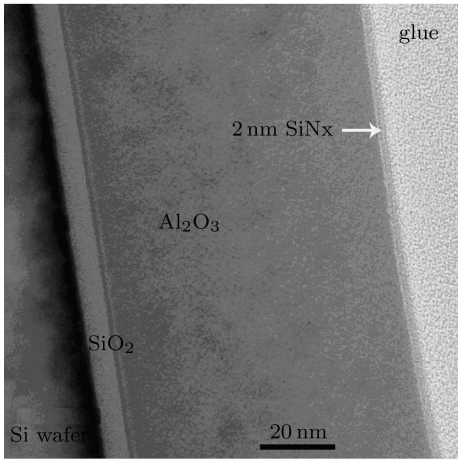


Fig.1. Cross-section TEM micrograph of the 2 nm a-SiN_x film.

Figure 2 shows the SEM surface morphology of samples immersed in oxalic acid solution [0.1 mol/L $HOOCCOOH{\cdot}2H_2O$] for 24 hours at room temperature. The white spots represent pinholes through which the etching solution attacked the underlying Si wafer substrate, as shown in Fig.2(a). For the a-Al_2O_3 substrate not covered with a-SiN_x film, the surface was covered by pinhole defects ($\sim166/mm^2$). However there is no visible corrosion marks on the surface of samples covered with the 2 nm ultra-thin a-SiN_x film, as shown in Fig.2(b). This suggests that the 2 nm a-SiN_x film should provide sufficient protection for the underlying layers from corrosion. The reference a-CN_x films deposited by magnetron sputtering by other research groups have not shown such properties.[1–4,9–12] Their results indicate that a-CN_x films with 2–4.5 nm thickness cannot provide sufficient protection for the underlying layers from corrosion, since such ultra-thin a-CN_x films inevitably contain pinholes and defect structures.

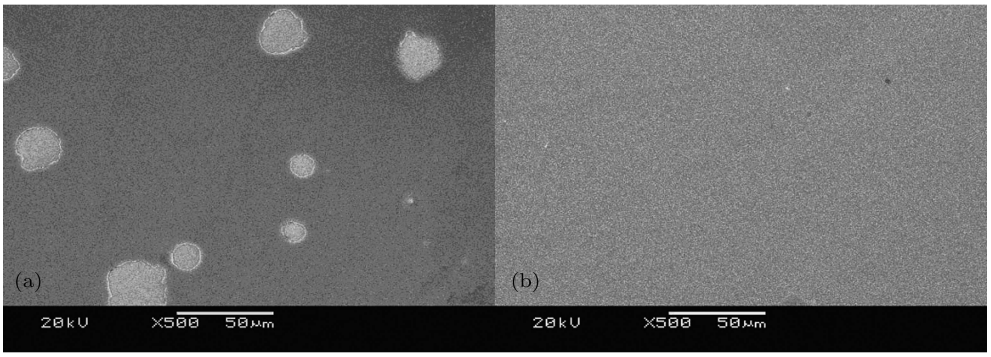


Fig.2. Surface morphologies after 24 h corrosion in oxalic acid solution: (a) no a-SiN_x film, (b) covered with the 2 nm a-SiN_x film.

3.2. The XPS analysis

In order to understand the relationship between the anti-corrosion performance and the bonding state of the Si atoms, the high-resolution Si 2p XPS spectra of a-SiN_x films are analysed, as shown in Fig.3. The full width at half-maximum value of the spectra implies the multiple bonding states of the Si atom. The deconvolution of the spectra with Gaussian peaks suggests the presence of three bonding states, giving the bonding energy values at 99.6, 101.7 and 103.7 eV, which could be attributed to Si-Si, Si-N, and Si-O bonding structures, respectively.[13,14] Figure 3 also gives the integrated area percent of each bonding state as well as the N/Si atom ratio in Si-N asymmetric stretching vibration bonding structures, calculated from the area and the atomic sensitivity factors.[15] From Fig.3, we can see that for a-SiN_x film, the content of Si-N bond reaches 94.8% and the N/Si ratio of the Si-N bond is equal to 1.33, as in the stoichiometry of Si_3N_4. The nano-indentation analysis indicates that the hardness of the a-SiN_x films reaches the highest value (25.0 GPa) with such stoichiometry, which corresponds well with the results of other researchers.[4,13,16–18] The a-SiN_x films contained only about 1.5% unstable Si-Si bonds which could easily be oxidized or broken by the oxalic acid solution. At the stoichiometry composition of Si_3N_4, the stable Si-N bonds are saturated so that the Si dangling bonds are minimized. Combining these two reasons, we conclude that the a-SiN_x films have such dense layer structures and excellent anti-corrosion properties.

3.3. Roughness analysis

Low surface roughness is another excellence of the a-SiN_x films deposited using our technique. For the purpose of investigating the influence of film thickness on surface roughness, ultra-thin a-SiN_x films with a thickness of 2, 10, and 15 nm were deposited on Si substrates. Figure 4 shows RMSR as a function of the film thickness. The RMS of the three samples was all less than 0.2 nm, which demonstrates that the three films were all atomically smooth, corresponding well with the above TEM results. Even when the thickness increases to 700 nm, the film was still atomically

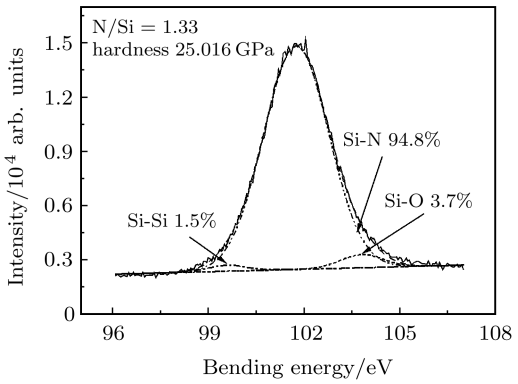


Fig.3. The XPS Si 2p spectra together with the deconvolution results and hardness data determined from the 300 nm thick films deposited on Si substrates.

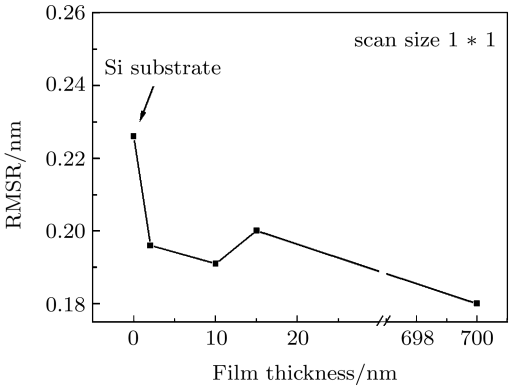


Fig.4. The RMSR of a-SiN_x films deposited on Si wafers.

smooth, with the RMSR less than 0.2 nm, as shown in Fig.4. The RMSR of all our samples was less than that of the Si substrate, which means that the surface roughness of the substrate can be improved by depositing ultra-thin a-SiN_x films with our technique. With the high hardness and low surface roughness, the ultra-thin a-SiN_x films display acceptable wear resistance properties, as discussed in our previous publication.

Inside typical magnetron sputtering plasmas, 95%–99% of the particles are neutral metastable atoms (Si*), and usually move in random directions.[3,16,17] However, there is an obvious Si^+ ion optical emission spectrum at 634.7 nm wavelengths in our MW-ECR PEUMS system, which means that there is some fraction of energetic Si^+ ions arising from the target and moving towards the substrate, as shown in Fig.5.[19] These Si^+ ions were accelerated by the RF bias voltage added on the substrate holder and bombarded the growing film surface with about 100 eV incident energy. The 100 eV was chosen as the incident energy because according to Kress *et al*[20,21] the Si^+ ions with lower energy do not effectively improve the growing surface morphology. We speculate that the growing surface is bombarded by these energetic Si^+ ions with appropriate incident energy, leading to more efficient momentum transfer and hence restraining the island growth.[3] For this reason, we have obtained 2 nm ultra-thin a-SiN_x films with a dense layer structure, an atomically smooth surface, and acceptable mechanical and corrosion properties.

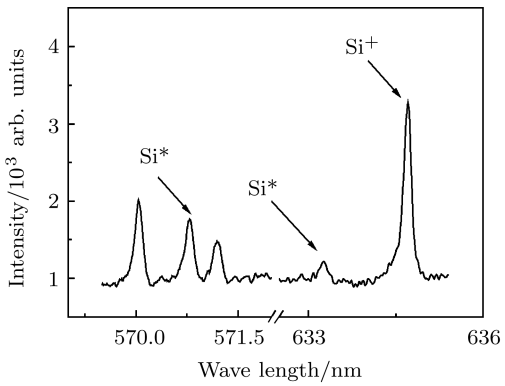


Fig.5. The OES peaks intensity of Si*, Si^+.

4. Conclusion

The next generation of protective overcoat must be atomically smooth and pinhole-free over large areas in order to provide the necessary corrosion protection for the underlying disk and read/write heads. For practical reasons, it would be most desirable to accomplish this with magnetron sputtering, because of the drawbacks of producing particles by FCVA,[1−5] and containing H element by chemical vapour deposition,[1−5] etc. Our works show that magnetron sputtering can produce 2 nm ultra-thin a-SiN_x overcoats with excellent properties. We believe that ultra-thin a-SiN_x overcoats would be one of the best choices for disk and read/write head overcoats in the future because of their superior performance.

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