

Silicon nitride thin films deposited by reactive gas-timing magnetron sputtering for protective coating applications

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ABSTRACT

Silicon nitride is a promising alternative to carbon based materials for protective coatings, owing to its compatibility with existing silicon-based microfabrication. The complexity of the fabrication processes and contaminations hamper fine-tuning to obtain desirable coating properties. We have explored the reactive gas-timing rf plasma sputtering technique for silicon nitride thin film deposition as an alternative method to fine-tune the film properties. The gas-timing technique controls the on-off sequence of the sputtering gas (Ar) and the reactive gas (N₂) during deposition. We focus this investigation to the effect of the Ar:N₂ gas timing ratio (10:0, 10:1, 10:3, 10:5, 10:7 and 10:10) on the composition, the morphology, the corrosion resistance, and the hardness properties of the films, in comparison to the films deposited by conventional reactive sputtering with Ar-N₂ gas mixture. These deposited silicon nitride films were characterized by Auger electron spectroscopy, Raman spectroscopy, and atomic force microscopy. The chemical resistance was measured by the electrochemical corrosion test in sulfuric acid, while the hardness properties were obtained by nanoindentation. The results reveal that although the nitrogen content in the films increases only slightly when the N₂ timing is prolonged, the corrosive current of the films decreases abruptly. A thin passivating oxidized layer is found to play a major role in the corrosion resistance. In contrast, the hardness properties exhibit a uniform variation with the N₂ timing. The gas-timing sequence may induce morphological changes the underlying silicon nitride films. The highest hardness obtained by the gas-timing technique almost doubles that produced by the conventional mixed gas sputtering. Thus the reactive gas-timing technique suggests a new route to selectively control the properties of silicon nitride films with minor modification to existing microfabrication processes. Copyright © 2015 VBRI Press.

Keywords: Hard coatings; silicon nitride; corrosion; plasma sputtering.



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Introduction

Many excellent properties of silicon nitride (Si₃N₄), such as high corrosion resistance, high hardness, high chemical and thermal stability, make it one of the key materials for protective and hard coating applications [1-5]. The

applications of silicon nitride thin films extend to many research fields with different functionality, including as a protective layer and a diffusion barrier in microelectronic devices [3-5], an ion sensitive membrane in pH sensors [6], a phosphor in light emitting devices [7], and biocompatibility for biomedical devices [8]. The compatibility of silicon nitride to the silicon-based microfabrication technology provides it with the competitive edge over other materials [7]. Silicon nitride coating may be fabricated by several processes, such as chemical vapor deposition (CVD) [5, 9-11]. These processes, however, often require high operating temperature and hazardous chemicals as the nitrogen source.

Plasma magnetron sputtering is an alternative route for silicon nitride fabrication, which offers a low temperature

operation, and high film adhesion [2, 12-14]. Despite these advantages, the research interest in plasma sputtering deposition of silicon nitride is becoming limited. One of the main reasons is that conventional plasma magnetron sputtering with a homogenous mixture of sputtering and reactive gases may cause changes in the composition of the sputtering target over time. A large scale production of silicon nitride with plasma sputtering may face difficulties in controlling the properties precisely and reliably.

A novel rf magnetron sputtering technique called “reactive gas-timing” with an on-off sequence of reactive and sputtering gases have been demonstrated in metal oxynitride thin film fabrication [15-18]. The technique offers a precise control of the properties and the composition of the films. The optical band gap of the indium oxynitride thin films fabricated with such technique may be selectively tuned over a wide range from 1.4 to 3.4 eV by the adjustment of the gas-timing sequence, yielding drastic colour differences [16].

In this research, a method to fine-tune the properties of the silicon nitride thin films has been explored via the reactive gas-timing rf magnetron sputtering system without substrate heating or substrate biasing. We focus on the effect of the on-off timing ratio of the sputtering gas (Ar) and the reactive gas (N₂) on the composition and the morphology of the deposited silicon nitride thin films, in conjunction to their anti-corrosion and hardness properties.

Experimental

Materials

Silicon nitride (SiN_x) thin films were deposited onto p-type Si(100) wafer (Siltronic) and glass (borosilicate glass) substrates by rf magnetron sputtering system (modified Edward Auto 500) with the reactive gas-timing of Ar and N₂ gases (99.999%, TSG) using a 99.999% silicon target (Kurt J Lesker). At the start of each run, the target was also cleaned by pre-sputtering with pure Ar. The substrates were ultrasonically cleaned in isopropanol alcohol (99.7%), acetone (99.8%, Carlo Erba), DI water (Millipore) and then dried by N₂ blow gun. For the anti-corrosion measurements, 96% sulfuric acid (H₂SO₄, Carlo Erba) was used to prepare a 1M solution.

Table 1. Sputtering parameters for SiN_x deposition by reactive gas-timing magnetron sputtering.

Deposition parameter	Condition
Base pressure	6.0 x 10 ⁻⁶ mbar
RF Power	80 W
Sputtering temperature	Room temperature
Ar flow rate	10.0 sccm
N ₂ flow rate	3.0 sccm
Ar timing	10.0 s
N ₂ timing	1.0, 3.0, 5.0, 7.0, 10.0 s
Film thickness	100 nm

Reactive gas-timing magnetron sputtering

For the reactive gas-timing sputtering, Ar and N₂ were introduced into the chamber in alternation, with different duration (Fig. 1). The sputtering conditions are listed in Table 1. The sequence started with Ar injection into the chamber for 10 seconds, followed by N₂ injection for a

different duration (1.0, 3.0, 7.0, and 10.0 s) according to each experimental condition. The glow discharge plasma was maintained throughout the sputtering process. The thickness of the deposited films was monitored by the quartz crystal microbalance to achieve the total thickness of approximately 100 nm for all deposited films. Silicon nitride films were also prepared by the conventional sputtering in a homogenous gas mixture with a continuous flow condition of Ar and N₂.

Characterizations

The surface morphology and the chemical composition of the deposited silicon nitride thin films were characterized by the Atomic Force Microscopy (AFM, Seiko SPI400) in the non-contact mode and the Auger Electron Spectroscopy (AES, ULVAC PHI700), respectively. The AES measurements were obtained from two depth levels: at the surface and at 10 nm below the surface after ion-beam etching to removal natural oxide layer. Raman spectroscopy (Thermo Scientific DXR Smart Raman) was also conducted on the samples to obtain the chemical bonding information and to complement the AES composition measurements. The anti-corrosion performance was measured by the electrochemical corrosion test (Autolab PGST AT302 Potentiostat) in 1M H₂SO₄ to obtain the I-V polarization curve (Tafel plot). The hardness and the elastic modulus of the silicon nitride thin films were characterized by nanoindentation (Micro Materials), with the load range of 0-1000 μN using the Berkovich tip.

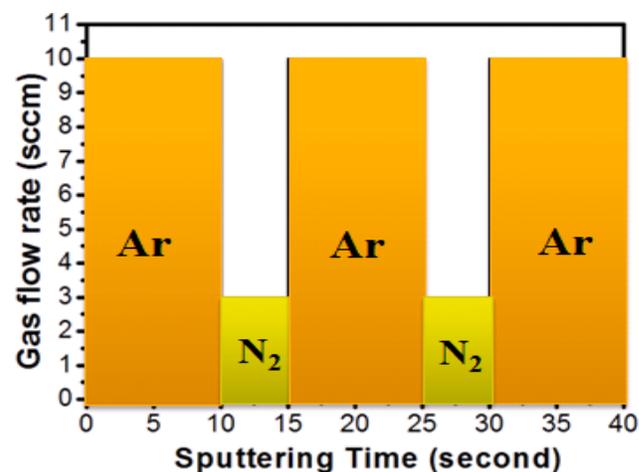


Fig. 1. Schematic of the Ar and N₂ gas-timing sequence during plasma sputtering. The graph depicts the flow rate for each gas as a function of time.

Results and discussion

Chemical compositions

Fig. 2 shows the N and Si atomic composition obtained by AES as a function of the N₂ timing with the fixed Ar timing of 10.0 s. Differences between the atomic compositions on the surface of the films (Fig. 2(a)) and at the depth of 10 nm (Fig. 2(b)) are apparent. The higher O content on the surface is expected from oxidation upon exposure to air. However, at the 10 nm depth, the O content drops

drastically. The remaining O presence in the films possibly originates from background gases in the sputtering system. Some background C was also detected in the films (not shown). This oxidized layer with thickness of less than 10 nm indicates that the layer acts a self-passivation, preventing further oxidation inside the films. This demonstrates a desirable characteristic for protective coating.

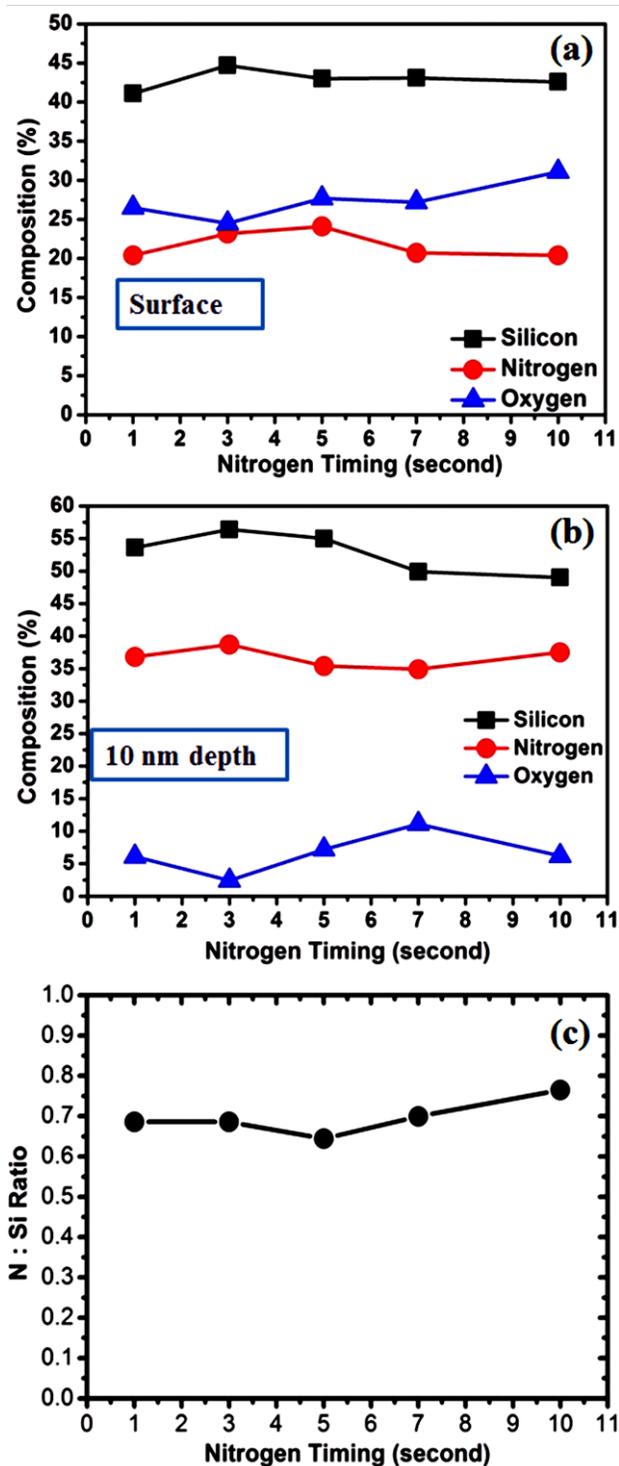


Fig. 2. N and Si composition obtained by Auger Electron Spectroscopy for the deposited silicon nitride films with different N_2 timing: (a) on the surface, (b) at 10 nm depth and (c) N/Si ratio at 10 nm depth.

As the N_2 injection duration during the reactive gas-timing sequence is prolonged, Fig. 2(c) indicates that the content of N in the sputtered films increases slightly with the N/Si ratios of approximately 0.65 – 0.75. The expected ratio of a pristine Si_3N_4 is 1.33. The lower N/Si ratios are expected from the low N_2 flow rate. The low flow is essential to maintain the plasma stability. In comparison, the atomic compositions of the conventional mixed-gas sputtering for Si, N and O at 10 nm depth are 44.2, 28.8, 21.7, respectively. This gives the N/Si ratio of around 0.65, which is at the low end of the gas-timing series. The high O content at the same depth level of 10 nm for the mixed gas sputtering may indicate the absence of the thin passivating layer.

The Raman results of the silicon nitride films deposited at different N_2 timing are shown in Fig. 3. The spectra displays distinct peaks around 550 and 1100 cm^{-1} , which is should be the Si-O phase from the broad shoulder. The $Si-N_x$ phase has been reported around 700-900 cm^{-1} [9], which is present in the spectra but as a rather weak feature. The Raman measurements were obtained by the laser backscattering, which is surface sensitive. The results should then be correlated to Fig. 2(a) for the passivation layer. This may also explain the distinct characteristic of the 10:10 sample, which has the highest surface O content. Nevertheless, these Raman spectra confirm the presence of $Si-N_x$ in the films.

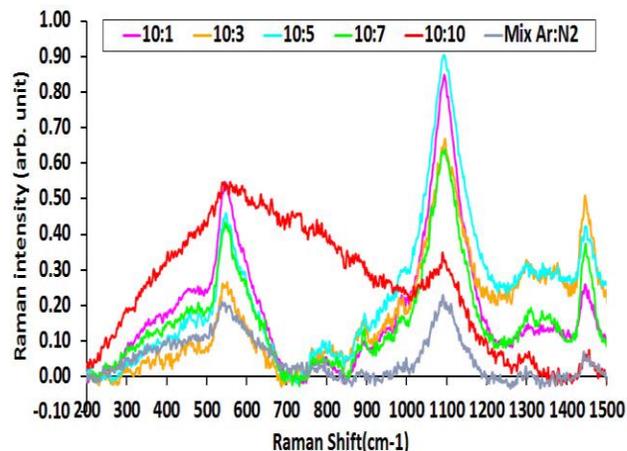


Fig. 3. Raman spectra of silicon nitride thin films deposited with different N_2 timing.

Surface morphology

The composition measurements indicate a marginal increase in the N content in the films as the N_2 timing is extended. It may well be expected that other properties of the films might not vary significantly. The AFM ($5 \times 5 \mu m^2$ area) results of the silicon nitride films on silicon substrates as shown in Fig. 4 suggest that this may not be the case. The surface of the films deposited at short N_2 timing appears rather smooth, whereas large features are observed in the case of long N_2 timing, as well as the mixed-gas sputtering. This is unlikely to be contamination, since the large features are present throughout the films. They are also not observed in the short N_2 timing case. These

features may occur as a result of the instability of the glow discharge plasma with an increase in the N_2 gas.

The root-mean-square (rms) surface roughness was calculated from the AFM results for $1 \mu\text{m}^2$ areas. The areas were selected to avoid the large features in the case of long N_2 timing, in order to compare the morphology of the underlying films. The results in **Fig. 5** exhibit a sharp increase for the Ar: N_2 timing ratio of 10:7. The rms roughness of the films prepared by the mixed gas sputtering is also measured to be $0.47 \pm 0.03 \text{ nm}$, which is much higher than those of the gas-timing series. The rms roughness results of the underlying surface are in agreement with the trend observed in the AFM images in **Fig. 4**. The long N_2 timing may indeed lead to an increase in the film roughness.

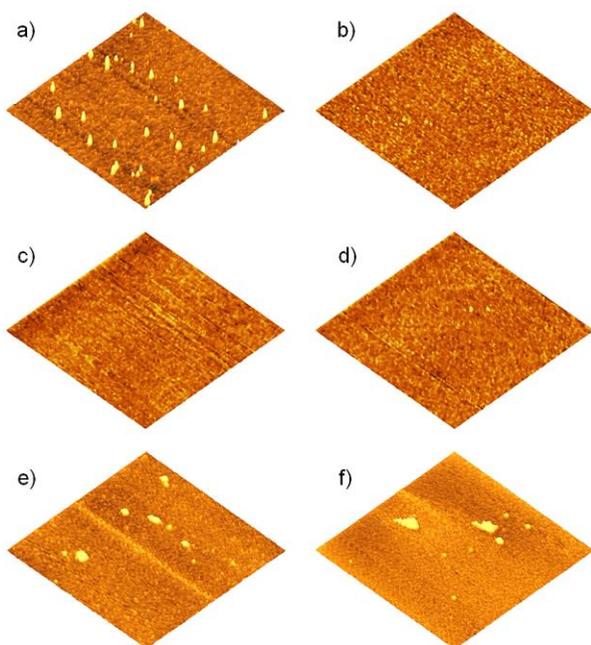


Fig. 4. AFM topographic images ($5 \times 5 \mu\text{m}^2$ area) of silicon nitride thin films deposited with different N_2 timing: (a) mixed Ar- N_2 , (b) 10:1, (c) 10:3, (d) 10:5, (e) 10:7 and (f) 10:10. All the images are set to same height scale.

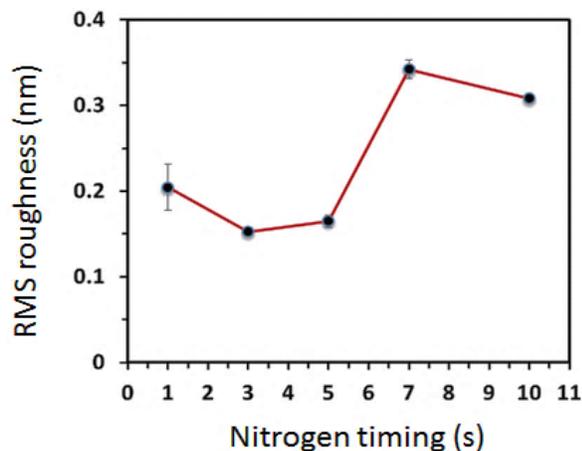


Fig. 5. Root-mean-square surface roughness ($1 \mu\text{m}^2$ area) of silicon nitride thin films deposited with different N_2 timing.

Corrosion resistance

Fig. 6 exhibits the results of the corrosion polarization test in the $1\text{M H}_2\text{SO}_4$ aqueous solution for the silicon nitride films deposited on the silicon substrates. The I-V polarization curves (Tafel plot) are shown in **Fig. 6(a)**. The corrosive current extracted from the curves as a function of the N_2 timing is depicted in **Fig. 6(b)**. The results show a rapid decrease in the corrosive current at short N_2 timing. The current is reduced by a few orders of magnitude above the Ar: N_2 ratio of 10:7 ratio.

The non-uniform variation in the properties of the films follows the trend as observed in the AFM results, which contrasts the gradual change in the N/Si composition. However, if we consider only the high surface roughness of the films deposited with long N_2 timing, the corrosive resistance is expected to diminish. This is indeed the case for the mixed gas sputtering with the corrosive current greater than 100 nA (not shown). As discussed in the AES results, thin passivation layers are formed on the surface of the gas-timing silicon nitride films. These layers are vital to the corrosion resistance of the films. It is highly possible that the gas-timing process may induce some morphological changes and more compact bonding within the films. Raman results in **Fig. 3** provide some indication that this may be the case. However, the Raman intensity level is subjected to many factors, the quantification using Raman spectra is rather difficult to obtain. Full stoichiometric studies of these gas-timing silicon nitride films are required.

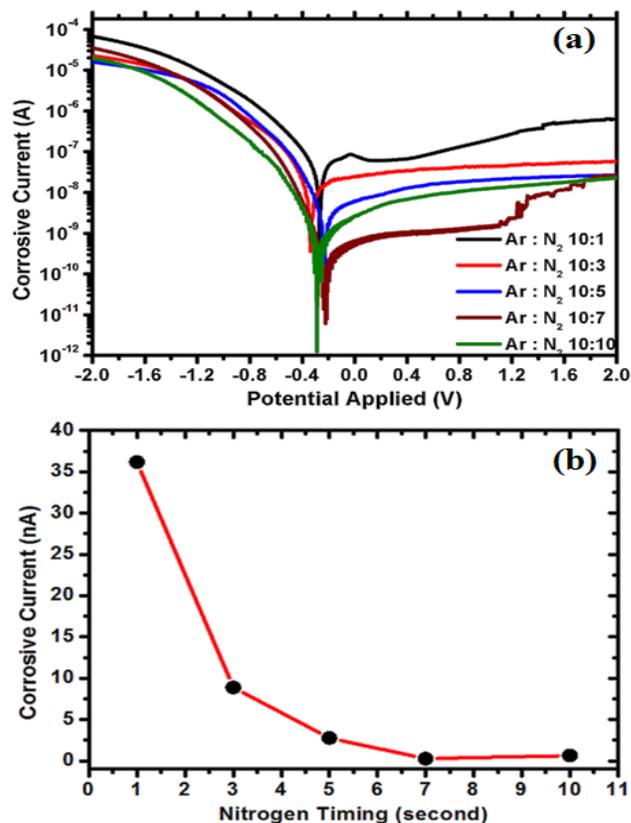


Fig. 6: Corrosion resistance of silicon nitride thin films deposited with different N_2 timing: (a) I-V polarization curve and (b) corrosive current as a function of N_2 timing.

Hardness properties

As of interest for hard coating applications, the mechanical properties of the silicon nitride thin films fabricated on silicon substrates was characterized by the nanoindentation technique. Fig. 7 displays the hardness and the elastic modulus as a function of the N₂ timing. The values were extracted from the load-displacement curve at the maximum load of 1 mN. As the N₂ timing is extended, the hardness of the silicon nitride films gradually increases, while the elastic modulus exhibits the opposite trend. In other words, at long N₂ timing, the films become stronger but less rigid. These gradual variations contradict the abrupt changes observed in the surface roughness and the corrosion resistance. This strongly suggests that the mechanical properties obtained by the nanoindentation reflect the properties of the underlying silicon nitride films, rather than the oxidized surface layers.

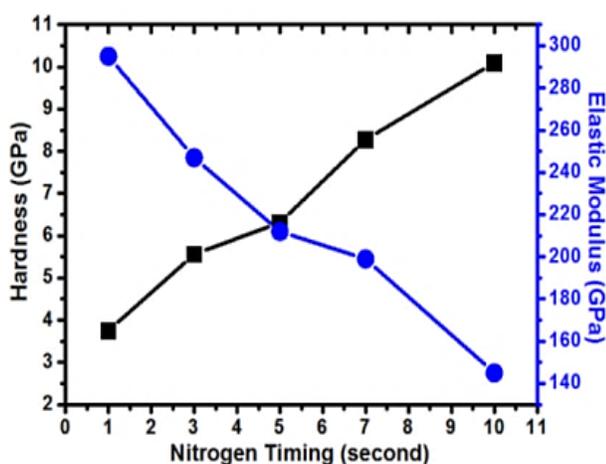


Fig. 7. Hardness and elastic modulus of the silicon nitride thin films deposited with different N₂ timing.

In comparison, the silicon nitride films obtained by the conventional mixed gas sputtering yield the hardness and the elastic modulus of 6.4 GPa and 297 GPa, respectively. This indicates a film with moderate hardness and high rigidity, which contrasts the apparent trend in the gas-timing series. This further suggests that the gas timing sequence may induce better N-incorporation and some structural properties that are distinctively different from the films obtained with conventional sputtering. One of the possibilities is a mixture of nanocrystalline and amorphous phases [19]. Another is an example of the multilayer structure obtained by chemical vapor deposition with a modulated sequence, similar to the reactive gas-timing approach [11].

Conclusion

This study suggests that the reactive gas-timing magnetron sputtering technique is able to produce the silicon nitride films with desirable properties for protective coatings that arise from two origins, namely, the thin oxidized surface layers and the underlying bulk-like layers. The oxidized layers are below 10 nm in thickness and are only observed in the case of the thin films in the gas-timing series, not in

those obtained by the conventional mixed gas sputtering. These layers, which exhibit large variations in their properties as a function of the N₂ timing, play a vital role in the corrosion resistance properties. In contrast, the underlying layers, which exhibit gradual compositional changes with the N₂ timing, lead to uniform variations in the hardness and the elastic modulus of the gas-timing silicon nitride films. The exact nature of the morphological changes leading to this variation in the mechanical properties of the films is a topic worth further investigation.

Overall, the reactive gas-timing magnetron sputtering technique is able to produce the silicon nitride films with properties that are different from the conventional mixed gas sputtering. This work also demonstrates that the on-off timing sequence of Ar and N₂ may be applied to selectively tune the chemical and mechanical properties of the silicon nitride films. The reactive gas-timing sputtering offers a novel route to fabricate silicon nitride coatings at low cost and with high precision and compatibility to existing technology.

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