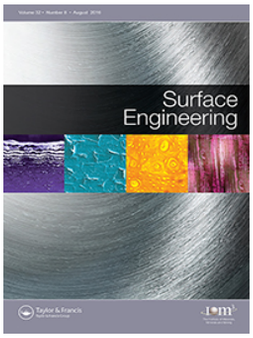

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Enhanced mechanical properties of HfO_2 film by nitrogen doping

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The chemical composition, structure and mechanical properties of hafnium oxide films with different nitrogen constituents were investigated. X-ray photoelectron spectrum analysis showed that nitrogen atoms acted as oxygen substitution and interstitial atoms. The crystalline features exhibited no change during nitrogen doping. Nevertheless, the films with high compressive stress displayed significantly enhanced mechanical properties. The enhanced mechanism could mainly be attributed to the dislocation obstacle motion by inserting nitrogen atoms.

Keywords: Hafnium oxynitride film, Magnetron sputtering, Stress, Nitrogen doping, Hardness

Introduction

Transition metal oxide/oxynitride thin films, due to the flexible constituent and promising properties, have attracted tremendous attention in both the scientific and technological communities over the past few years. Briefly, they could be applied to well-known tribological areas, including cutting tools and turbine blades because of super hardness and chemical stability;[1] they have been considered as optical coatings due to multispectral transmittance and low absorption,[2] and as promising insulating materials owing to high permittivity[3] and as ferroelectric materials.[4] As for the group of oxynitride materials, numerous researchers paid more attention on titanium oxynitride,[5–7] zirconium oxynitride,[8,9] hafnium oxynitride[10,11] and tantalum oxynitride.[12,13] Among them, hafnium oxynitride film has become one of the most fascinating films due to their peculiarly multifunctional properties.[14–21]

Various processes including reactive magnetron sputtering,[15,22] ion beam assisted deposition[18] and chemical vapour deposition[16] have been adopted to prepare hafnium oxynitride films. One of the most important and promising applications is the super mechanical properties of oxynitride films, which closely dependent on nitrogen content. However, it is difficult to obtain oxynitride films with a high fraction of nitrogen due to the strong and preferred O–M bond than N–M bond. To our best knowledge, studies regularly limited to the chemical composition, microstructure and mechanical properties of hafnium oxynitride films with different nitrogen contents.

In this work, we investigated the mechanical properties of hafnium oxynitride films with different nitrogen contents. Based on the characterisation of chemical composition and structures of films, the film stress and mechanical properties have been measured and correlated to the intrinsic factors.

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Experimental details

The hafnium oxynitride films were prepared on Si(100) substrate by radio frequency magnetron sputtering using a metallic hafnium target (99.99% purity) with the reactive gas ratio of $N_2/(N_2 + O_2)$ from 0.5 to 1. This reactive gas ratio can be realized by increasing the oxygen flow rate from 0 to 40 sccm and fixing the nitrogen gas flow at 40 sccm during deposition. Other growth parameters remained constant, including the argon flow rate of 50 sccm, the distance between target and substrate of 75 mm, the power of 120 W, and the total pressure of 1 Pa. The deposition time was 1 hour for all the samples, the film thickness varied from ~108 to 128 nm as the oxygen gas increases from 0 to 40 sccm during deposition.

High resolution X-ray photoelectron spectroscopy (XPS, PHI ESCA 5700) was used to determine the film composition with Al Kα radiation at 1486.6 eV. The structure was evaluated by GIXRD (X' Pert-Pro) with Cu Kα radiation source ($\lambda = 1.541$ Å) at the incident angle of 1.5°. The stress of films was calculated by Stoney equation, using the curvature and thickness measured by profilometry. The hardness and elastic modulus of the films were evaluated by Nanoindenter XP with continuous stiffness measurement mode. This instrument monitors and records the dynamic load and displacement of the three-sided pyramidal diamond (Berkovich) indenter with a tip radius of about 40 nm during indentation with a force resolution of about 50 nN and displacement resolution of about 0.1 nm. The indentation depth is 430 nm for each sample. The hardness and modulus values were chosen as the real hardness and modulus of films when the indentation depth is in the around 10 times less than film thickness.

Discussion and results

The composition and chemical bonds of as-deposited films were evaluated by XPS, which are shown in Fig. 1.

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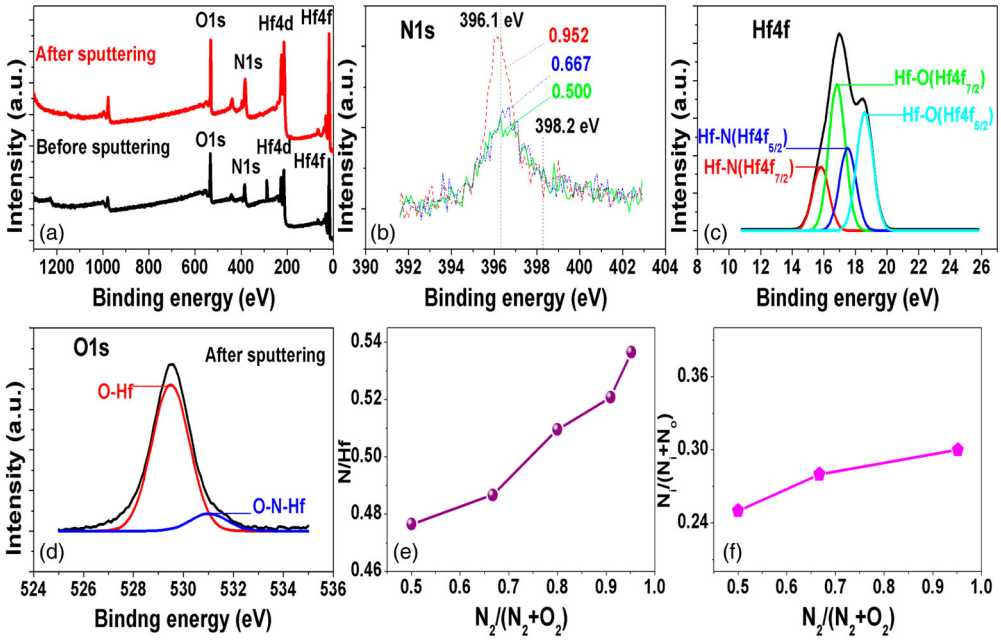
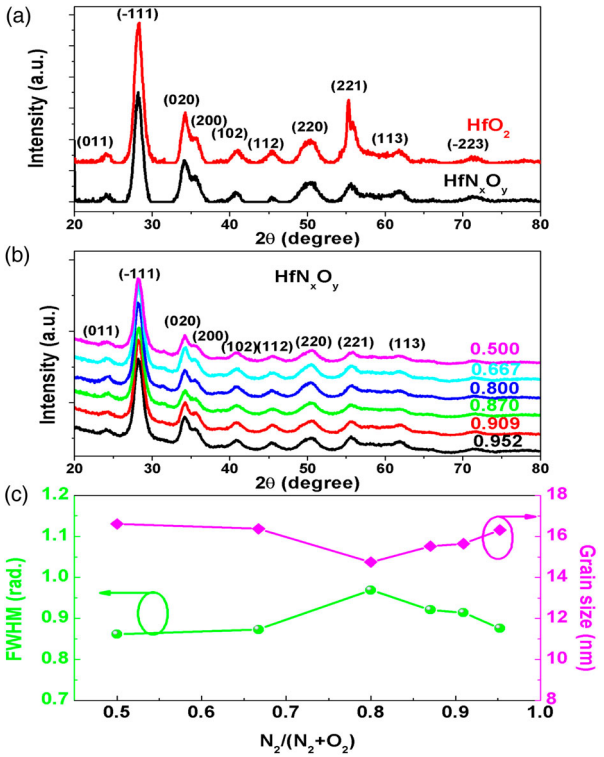


1 The survey XPS spectra of films at $N_2/(N_2 + O_2)$ ratio of 0.952 before and after sputtering for 5 minutes *a*; the core level of N1s spectra of films at $N_2/(N_2 + O_2)$ ratio of 0.5, 0.667 and 0.952 after sputtering *b*; the core level spectra of Hf4f at the ratio of 0.952 *c*; the core level spectra of O1s of films at the ratio of 0.87 *d*; the ratio of *e* N/Hf and *f* $N_i/(N_i + N_o)$ as a function of $N_2/(N_2 + O_2)$ ratio

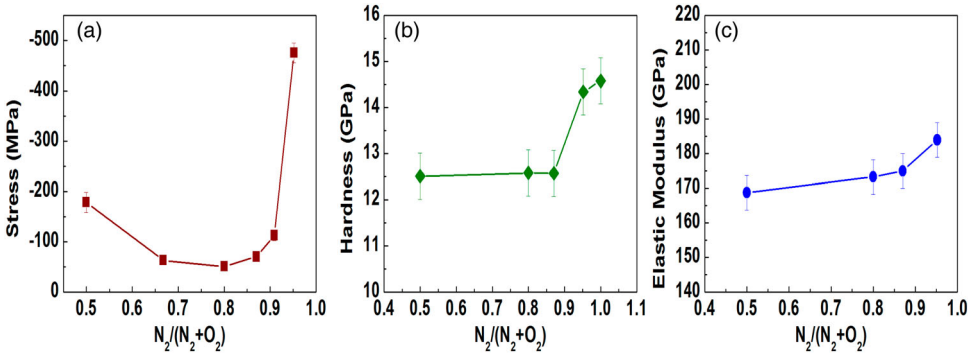
Figure 1*a* exhibits the survey spectra of films at $N_2/(N_2 + O_2)$ of 0.952 before and after argon ions sputtering for 5 minutes. It is clear that the strong peaks come from N, O, Hf and the adventitious elements exist in the films regardless of sputtering. Figure 1*b* displays the XPS spectra of N1s at different N_2 flow rates after sputtering for 5 minutes. The nitrogen content increases in the films as the nitrogen gas increases. Due to 5 minutes sputtering and etching, absorbed nitrogen from the exposed air has a slight influence on film composition. According to GIXRD patterns (see Fig. 2), there is no peaks from HfN phase, meaning no HfN phase formation as the nitrogen increases. Thus, it is reasonably speculated that the nitrogen exists in two chemical states, i.e. interstitial one (expressed as N_i) and substituted one (expressed as N_o). According to the asymmetry of N1s peak, the N1s peak can be deconvoluted into two peaks located at 396.1 eV and 398.2 eV, corresponding to Hf–N–Hf bond (N_i) and Hf–N–O bond (N_o),[23] which is similar to the nitrogen doping yttrium oxide and titanium oxide films.[24,25] The N1s binding energy of the latter site is about 2 eV higher than that of the former due to more negative charge of N residing in the latter site. The spectra of Hf4f core level were shown in Fig. 1*c*. The Hf4f can be deconvoluted into two doublet peaks due to the spin-orbit splitting (Hf4f7/2 and Hf4f5/2), the first pair is located at 15.8 and 17.5 eV corresponding to the Hf–N bond,[10] it shifts to a higher binding energy by ~0.5 compared with the reported Hf–N bonding energy,[26] the others are located at 16.8 and 18.4 eV in consistence with Hf–O bond, which shifts a lower binding energy compared with Hf–O binding energy in HfO_2 films.[10,27] The shift of binding energy is due to the nitrogen incorporation into the films, which has confirmed the nitrogen bonds again. Similarly, the spectra of O1s of films at nitrogen flow ratio of 0.8 reveal the trend as shown in the Fig. 1*d*. The nitrogen incorporation causes the lower shift of



2 The GIXRD patterns of *a* HfN_xO_y films at the N_2 flow rate of 0 and 40 sccm and *b* HfN_xO_y films as a function of $N_2/(N_2 + O_2)$ ratio; c the FWHM and grain size of films as a function of $N_2/(N_2 + O_2)$ ratio

Hf–O bond due to the more negative charge.[28] The peak (~531.1 eV) is believed to be the Hf–N–O bond.

The calculated ratio of N/Hf is plotted in Fig. 1*e*, as the ratio increases, the ratio of N/Hf increases from 0.48 to



3 The stress *a*, the hardness *b* and modulus *c* of HfN_xO_y films as a function of $N_2/(N_2 + O_2)$ ratio

0.54, indicating that the N content increases in the films. For the variation of N_i and N_o as the nitrogen content increases, Fig. 1*f* gives the ratio of interstitial N atoms to the total N atoms, showing the increased tendency and indicating more content of interstitial N in films at higher nitrogen atmosphere.

Figure 2*a* shows the crystalline structures of films prepared at N_2 flow rate of 0 and 40 sccm corresponding to HfO_2 film and HfN_xO_y film. There is no HfN phase formation. Such interstitial N and other substituted N cannot change the Hf–N bonds arrangement to form HfN phase due to the similar radius between N and O atoms. Consequently, the GIXRD patterns of HfN_xO_y films at different rates from 0.5 to 0.925 show the same case (in Fig. 2*b* and *c*). The structural stability through incorporating nitrogen is also verified by theoretical calculation.[29]

The residual stress of films was calculated by Stoney equation through measuring the film thickness and the curvature of film-substrate by profilometry.[30] The modulus and Poisson's ratio of silicon substrate are 202 GPa and 0.27, respectively. All the deposited films have compressive stress. Figure 3*a* shows the stress of films grown at different $N_2/(N_2 + O_2)$ ratios, which is in the level of MPa. As the reactive nitrogen gas increases, the stress first slightly decreases to ~50 MPa, and subsequently abruptly increase occurs to 478 MPa. The compressive stress of films is generally recognised to be originated from energetic particles bombardment during film deposition.[31] In this work, the nitrogen incorporation mainly plays a role especially from the interstitial N atoms. The deposited films are polycrystalline; the N interstitial atoms could take up in grains and grain boundaries. Nitrogen atoms favourably arrange in boundaries, because the weak reactivity and the relief of defects.[32] Therefore, with the increase of nitrogen atoms in films, the interstitial nitrogen atoms cause large compressive once larger than the threshold shown in Fig. 3*a*.

Figure 3*b* and *c* displays the hardness and modulus of HfN_xO_y films. It is clear to observe that the hardness maintains a lower constant (~12.5 GPa), when the $N_2/(N_2 + O_2)$ ratio reaches at 0.925, the hardness abruptly increases up to 14.5 GPa in Fig. 3*b*. In this work, nitrogen content and stress are the dominant change. It seems that the nitrogen content and accordingly high stress contribute the enhanced hardness. Indeed, several reports have showed the similar correlation between stress and hardness in TiN_xO_y films,[33] N doped WC films[34] and TiN_xC_{1-x} films.[35] The incorporated nitrogen in films could contribute the strengthened hardness. The substituted atoms (the N–Hf bond) has more covalent than O–Hf and thus has strong bond energy,[36] while it has less influence on stress. However, the interstitial atoms mainly exist in grain boundaries, giving rise to pronounced strain hardening results, which acts as an obstacle for dislocation motion.[33,35,37–39] The elastic modulus of such material is proportional to that of the hardness according to the Griffith theory.[40]

Conclusion

Nitrogen doped hafnium oxynitride films were realised by R.F. magnetron sputtering at the mixture atmosphere (oxygen and nitrogen). The composition and chemical bonds of HfON films were determined by XPS. Nitrogen content increases with the input nitrogen gas and the nitrogen atoms show the interstitial and substituted atoms in the films. Although nitrogen doping has no influences on the structures, the stress measurements indicate the obvious relation to the nitrogen contents. The enhanced hardness can be obtained at high concentration nitrogen doping. The increasingly distorted energy by interstitial nitrogen mainly contributes the largely enhanced hardness of HfN_xO_y films. This present work can provide the useful guide for engineering applications.

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