

# The effect of thickness and loading force on wear behavior of HfO<sub>2</sub>

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**Abstract.** The effect of annealing treatment on hafnium oxide (HfO<sub>2</sub>) thin films with two thicknesses (20 and 50 nm) has been observed. The surface morphology and tribological properties of HfO<sub>2</sub> thin films were measured through atomic force microscopy (AFM). It is found that annealing treatment and increasing thickness of thin film would promote the formation and growth of island-like grains, which contributes a raise in surface roughness. During scratch test, plowing behavior dominated the deformation mechanism in the form of lumps along the edge of grooves by AFM-3D images. Besides, slower scratch speed led to larger deformation energy and caused a serious fracture. The annealing-induced crystallization resulted in reduced penetration depth and coefficient of friction (COF). The varied COF with respect to different normal forces reflected substrate effect. The thicker HfO<sub>2</sub> films exhibited better wear resistance regardless of annealing conditions. It is because that increase in film thickness accompanied growth of polycrystalline structure.

## 1. Introduction

There are many applications based on hafnium oxide (HfO<sub>2</sub>) because of its unique chemical and physical properties such as high chemical stability, hardness [1], and thermal stability. In semiconductor industry, it is increasingly difficult to reduce the gate leakage and the tunneling current in the SiO<sub>2</sub> and SiON layer for the state-of-the-art and future nanotechnology nodes as the device feature size gets smaller and smaller. Therefore, HfO<sub>2</sub> based gate dielectric materials becomes the main components allowing improvement in the miniaturization of advanced integrated circuits, particularly complementary metal oxide semiconductor devices [2-4]. Although detailed studies exist on the electrical characterisation of HfO<sub>2</sub>, its mechanical properties still need to be investigated. While the thickness of thin films has shrunk from micrometer to nanometer range for achieving the need of miniaturization of electronic devices, it would accompany with the varied structure of material, which changes morphology and nano-mechanical properties such as surface roughness, wear resistance, and fatigue [5,6]. Furthermore, annealing treatment usually accompanies with changes of thin films structure like phase transition and relaxation [7,8]. Consequently, cyclic thermal stress and wire bonding-induced stress during the semiconductor processing could possibly damage the films, and thus lower the structure reliability, if nano-mechanical properties of HfO<sub>2</sub> thin films are not fully understood.

Nanoindentation technique is frequently used to measure the nano-mechanical properties of thin films such as hardness and Yong's modulus [9,10], it is difficult to remove substrate effect while film shrinks to nanoscale [11,12]. Nanoscratch technique can avoid this difficulty encountered in



nanindentation and is well suited for characterizing practical adhesion failure of thin films and coatings. The wear resistance of thin film can also be accessed through elastic deformation and pileup [13]. Under controlled scratch length and scratch speed, the residual penetration depth, coefficient of friction (COF) can be measured and assessed for the surface hardness and wear characterization under varied normal force and annealing temperatures.

In previous results, the thermal treatment-induced crystallization can enhance surface hardness of HfO<sub>2</sub> thin films by nanoscratch technique [14]. In this study, the effect of not only thermal treatment but also films thickness on the surface hardness of HfO<sub>2</sub> thin films was discussed. Furthermore, the crystallization of thin films can be reflected on surface morphology. For these reasons, the morphologies of as-deposited and annealed HfO<sub>2</sub> thin films with thickness of 20 and 50 nm were scanned by atomic force microscope (AFM). Nanoscratch experiments were also executed by AFM in lateral force measurement mode, in which a diamond coated tip was used to scratch HfO<sub>2</sub> thin films surface. The deformation mechanism was assessed by measured groove morphologies and cross-section scratch profiles. In addition, the coefficient of friction (COF) was evaluated using a combination of normal and lateral forces. The reliability of HfO<sub>2</sub> thin films deposited on Si wafer was assessed for semiconductor applications based on the evaluation of surface hardness and wear resistance.

## 2. Experiments

The method of preparing HfO<sub>2</sub> thin films has been described in previous study [14]. Firstly, the HfO<sub>2</sub> layers were grown on 8-inch (1 0 0) p-type Si wafers by using atomic layer deposition (ALD, Polygon 8200, ASM, USA) method that makes atomic scale deposition control possible due to the characteristics of self-limiting and surface reactions. Detail illustration of ALD process can be found elsewhere [15]. During the process, alternating surface saturating reactions between hafnium tetrachloride (HfCl<sub>4</sub>) and water (H<sub>2</sub>O) precursors at 300 °C were performed. Since no cleaning process before the deposition was applied to the bare Si wafer, a native SiO<sub>2</sub> thin layer existed between HfO<sub>2</sub> and Si wafer. The SiO<sub>2</sub> interface was not significantly affected by the ALD process. The as-deposited HfO<sub>2</sub> thin film was then cut into 20 mm × 20 mm samples for the subsequent annealing process. The annealing process was performed by rapid temperature annealing (RTA) method for 2 minute at 900 °C with a heating rate of 50 °C /sec under an argon environment. There has a potential crystalline phase transition and changes in crystallite sizes of HfO<sub>2</sub> thin films under the selected annealing temperatures [16].

For the nanoscratch tests, AFM (Dimension Icon, Bruker, USA) was used to perform the experiments. A nanoscale scratch on the HfO<sub>2</sub> thin film surface was obtained using a diamond-coated Si tip (DT-NCHR, Nanosensors, USA). This coating on tip features with extremely high wear resistance due to the unsurpassed hardness of diamond. The tip radius of curvature is ~100 nm on a 10- $\mu$ m-tall triangular pyramid probe. As far as mechanical specification is concerned, the probe includes a spring constant of ~42 N/m and a resonance frequency of ~330 kHz. The scratches were carried out with constant normal loads of 8, 24, 40, and 56  $\mu$ N. The length of each groove was 2  $\mu$ m. The scratching direction was perpendicular to the direction of cantilever length. At the same time, the lateral force was measured in situ through lateral force mode [17].

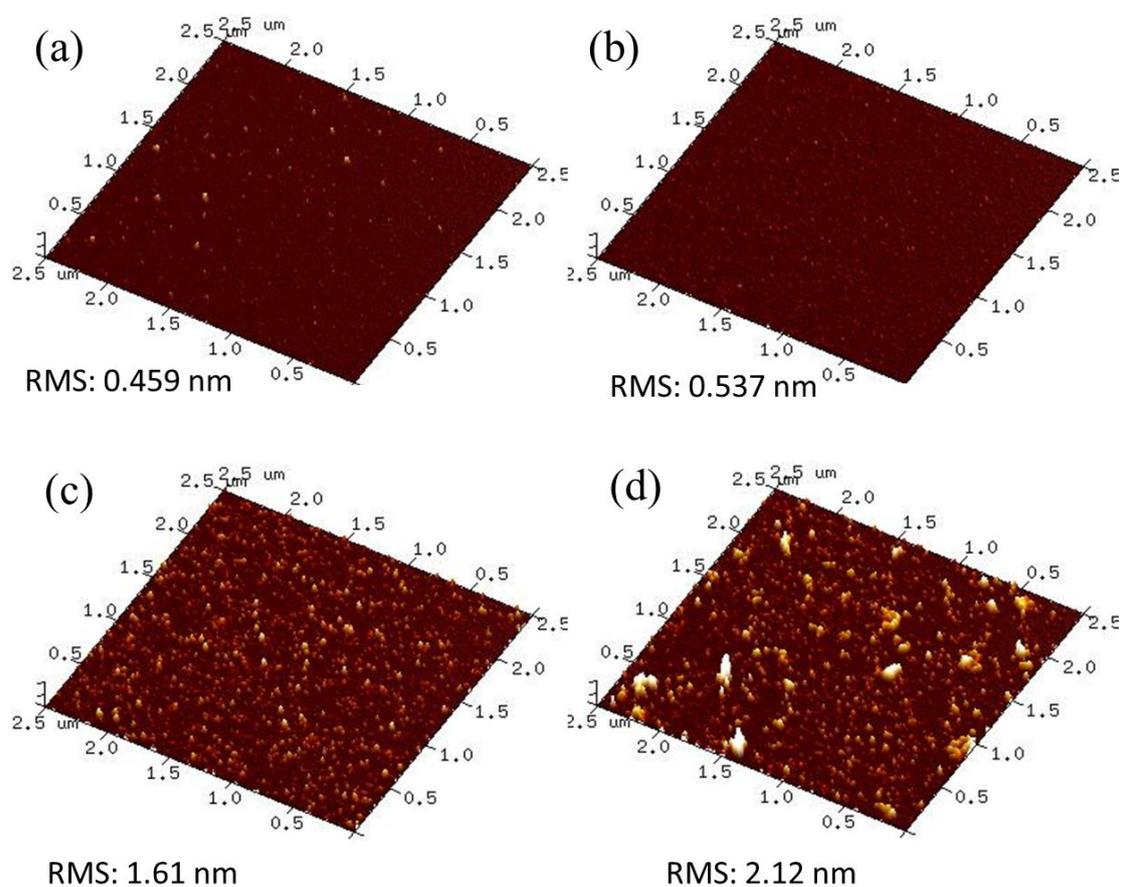
The surface morphology were probed using a SiN tip (SCANASYST-AIR, Bruker, USA) in peak force tapping mode to prevent additional damage to the groove. The pyramid shape SiN tip had a typical tip radius of 2~12 nm with a spring constant of ~0.4 N/m and a resonance frequency of 70 kHz. The surface hardness of the as-deposited and annealed HfO<sub>2</sub> thin films was characterized by the analysis of the scratch depths.

## 3. Results and Discussions

### 3.1. Surface property analysis

Figure 1 shows the morphology of HfO<sub>2</sub> thin films. It is obvious that the as-deposited HfO<sub>2</sub> thin films with 20 nm in thickness exhibited a flattest surface with low island density and minimum root mean square (RMS) surface roughness of 0.459 nm. The surface became rougher due to an increase in island

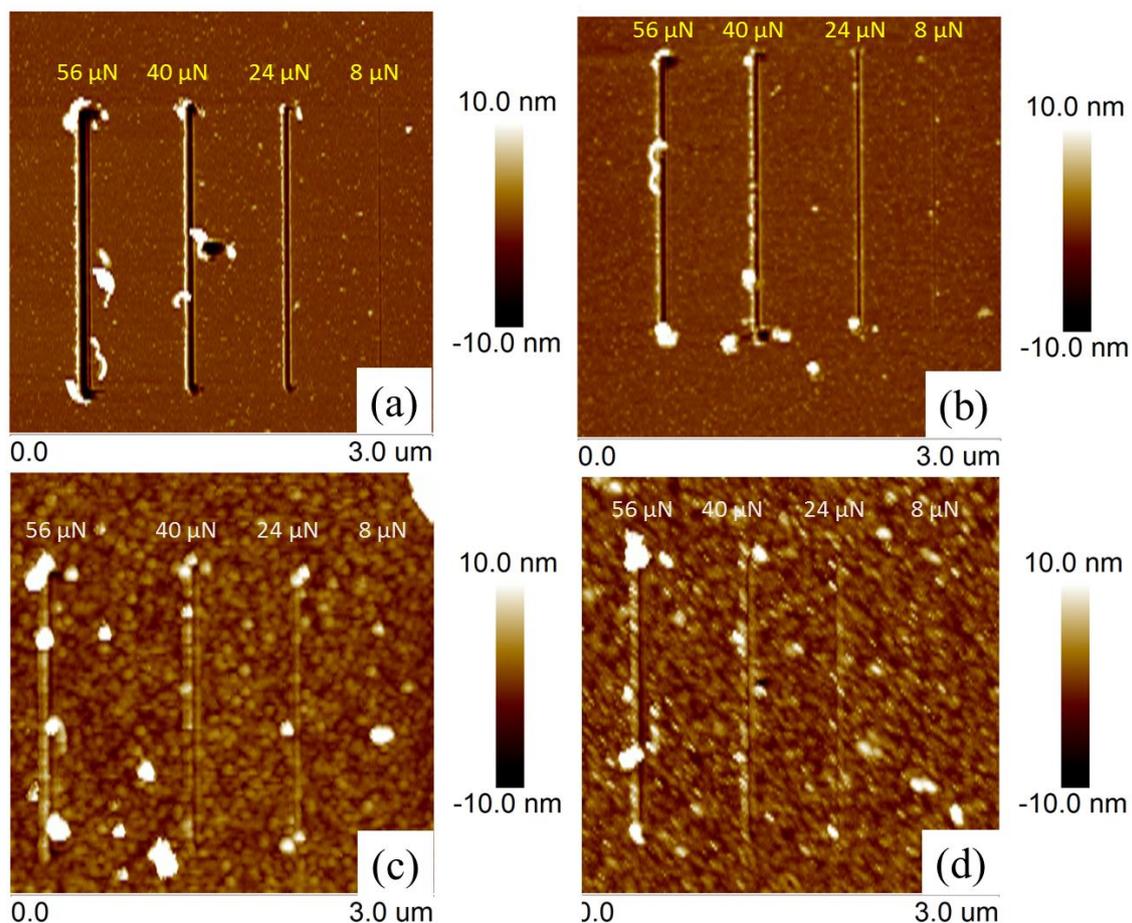
density after 900 °C annealing. According to previous research [18], there has a crystallization process from amorphous to polycrystalline structure with appropriate thermal treatment. As thin films thickness increased to 50 nm, more islands emerged which brings significant increase in roughness. It is because the  $\text{HfO}_2$  thin films structure is closely dependent on the film thickness. The nucleations of other growth directions are increased and the grain growth is expanded as the film thickness is increased [19]. The defects formed at the film growth at low temperature may provide nucleation sites for crystalline growth. Besides, the increase of the stress with the film thickness can contribute to the change in structure, which means relatively lower crystallization energy is required. It is also found that annealing treatment promote more crystallization of 50 nm thin films and can be proved by rougher morphology.



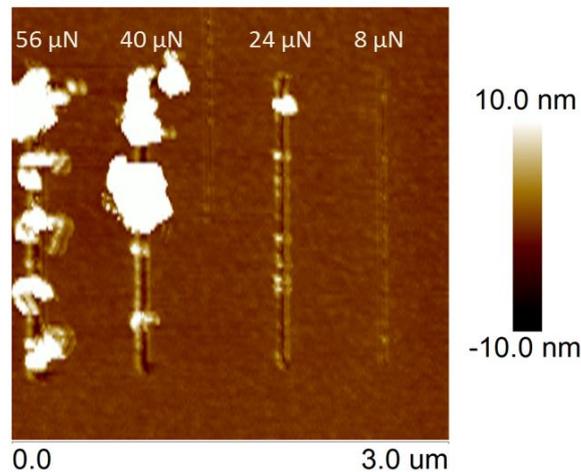
**Figure 1.** AFM-3D surface morphology of (a) as-deposited and (b) 900 °C-annealed  $\text{HfO}_2$  thin films with 20 nm in thickness, and (c) as-deposited and (d) 900 °C-annealed  $\text{HfO}_2$  thin films with 50 nm in thickness.

The surface hardness of the  $\text{HfO}_2$  thin films can be evaluated through the volume of the removed material using scratch technique. Figure 2(a) shows the AFM image of scratch topographies for as-deposited  $\text{HfO}_2$  thin films with 20 nm in thickness under different normal forces. It was found that lumps appeared along the two sides of scratch groove and became significant as normal force increased. The formation of lumps was a plastic deformation mechanism that the surface material

underwent a plowing behavior by AFM tip as a result of pileups on the groove edges. Furthermore, the degree of plastic deformation is proportional to the volume of lump [20]. Hence, the plastic deformation became significant accompanying with larger normal force from increased lump. It is worth noting that there was no agglomerated continuous ribbon-like debris and only a small amount of wear plate-like debris around the grooves. It means that  $\text{HfO}_2$  thin films exhibited good scratch resistance and high fracture strength under normal force range from 8 to 56  $\mu\text{N}$ . It also indicates that the material removal mechanism is primarily based on plowing behavior, but not cutting behavior and brittle fracture [21]. Figure 2(b) shows AFM images of scratch topographies for  $\text{HfO}_2$  thin films with 20 nm in thickness after 900 °C annealing. It is found that the plowing behavior still dominated on annealed samples and less debris was observed comparing with as-deposited one. However, the scratch grooves became narrower under all normal forces after annealing treatment. In addition, the scratches grooves were more unobvious on 50 nm thin films, as seen in figure 2(c) and (d). It indicated both thermal treatment and increase in film thickness can enhance the wear resistance. In addition, scratch speed effect on tribological properties was discussed. Figure 3 shows the scratch topographies for 20-nm-thickness thin films with 0.2  $\mu\text{m/s}$  scratch speed. Compared with Figure 2 in which scratch speed of 2  $\mu\text{m/s}$  was executed for all the scratches, the larger plate-like debris was observed on the scratch groove. This seems that AFM tip supplied more deformation energy to the surface materials at slower scratch speed and caused a serious fracture.



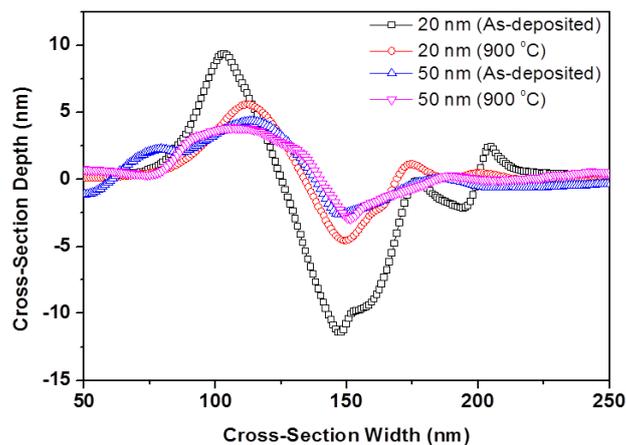
**Figure 2.** AFM-2D images of scratches on 20-nm-thick  $\text{HfO}_2$  films under (a) as-deposited and (b) 900 °C- annealed condition and 50-nm-thick  $\text{HfO}_2$  films under (c) as-deposited and (d) 900 °C-annealed condition.



**Figure 3.** AFM-2D images of scratches on 900 °C annealed HfO<sub>2</sub> thin films (20 nm in thickness) with 0.2 μm/s scratch speed.

### 3.2. Cross-section analysis of scratches

Figure 4 shows the cross-section profiles of scratch depth under 56 μN normal force. Compared with minimum scratch depth (~2.5 nm) in this experiment, the roughness is small enough to be ignored. In 20 nm samples, the groove depth obviously decreased after annealing treatment. From previous study [14], the crystallization process from amorphous to polycrystalline structure would increase surface hardness. In addition, amorphous structure force contributed to relative significant pileups due to plowing behavior. There has a further decrease in groove depth while HfO<sub>2</sub> thin films thickness increase from 20 to 50 nm, which proves that the thicker HfO<sub>2</sub> thin films exhibited better surface hardness either in as-deposited or annealed state due to polycrystallization.



**Figure 4.** Cross-section profiles of AFM scratches at 56 μN normal forces on as-deposited and 900 °C-annealed HfO<sub>2</sub> thin films with 20 and 50 nm in thickness.

### 3.3. Coefficient of friction

The COF is the relation between normal and lateral force [21,22]. In figure 5, the COF for annealed surface is smaller than as-deposited one for both 20 and 50 nm samples under all normal forces, indicating that crystallization by annealing treatment can enhance the wear resistance [14,22]. In addition, the COF increased at maximum normal force for as-deposited samples with both 20 and 50 nm thickness, which was due to substrate effect [23]. This effect reduces the hardness while hard thin films ( $\text{HfO}_2$ ) was deposited on soft substrate (Si), and also lowers the wear resistance. However, there has no same tendency on annealed samples and COF even decreased under maximum normal force. It is due to the formation of  $\text{HfSi}_x\text{O}_y$  layer, which possesses higher hardness than  $\text{HfO}_2$  thin films [14]. Therefore, the annealed samples can keep and even exhibit higher wear resistance. It also can be observed that thicker films has lower COF. The results can be contributed to higher degree of crystallization of thicker films than thinner ones.

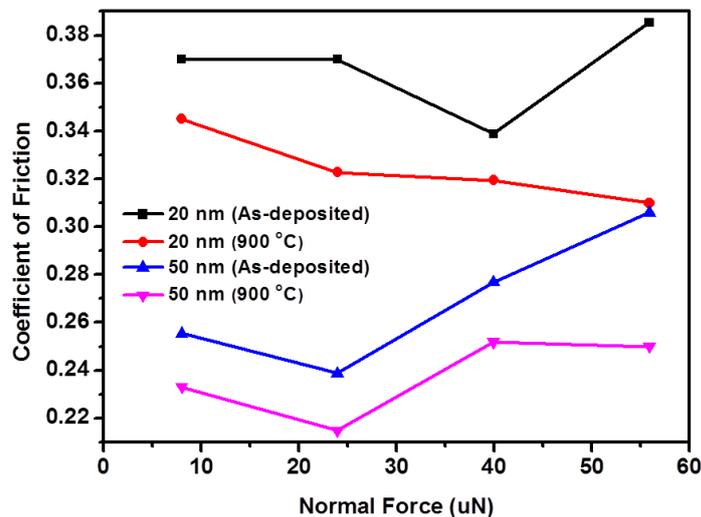


Figure 5. The normal force with respect to COF.

## 4. Conclusion

The structure of mechanical behaviors of  $\text{HfO}_2$  thin films with different films thickness, normal forces, and thermal treatments were investigated through morphology and nanoscratch tests with AFM system. The groove morphology, depth cross-section, and COF were considered for evaluating the phase transition, material removal mechanism, surface hardness, and wear resistance. From AFM images, rougher surface can be observed through annealed and thicker samples due to crystallization of  $\text{HfO}_2$  thin films. Lump along the scratch groove without the ribbon-like debris denoted that plowing behavior dominated the plastic deformation. Besides, low scratch speed made significant fractures due to large deformation energy. It was found that the scratch depth can be affected by annealing treatment and film thickness, which means that the structure transformation from amorphous to polycrystalline phases can enhance the surface hardness of the  $\text{HfO}_2$  thin films. Compared with as-deposited and thinner sample, lower COF and scratch groove of annealed and thicker ones under the same normal forces condition were also attributed to the annealing-induced crystallization which increased the wear resistance.

### Acknowledgements

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