

# Chapter 2

## A Thin Oxide Formation by Ozone Water Treatment

### 2.1 Introduction

As integrated circuits have been aggressively scaled down to nano-meter, the high-k materials will be applied to replace silicon dioxide as gate dielectric in the future. However there are many issues when high-k materials directly contact on Si. It is fact that a thin SiO<sub>2</sub>-like layer is inevitable. Therefore, an ultra thin SiO<sub>2</sub>-like layer is necessary to deposit on Si surface prior to high-k material deposition. This critical interfacial layer will play an important role in device performance.

With the present UVO<sub>3</sub>CVD technique [24], the minimal layer thickness or rather the amount of silicon dioxide which can be applied is less than 1 Å or 0.4 part of a monomolecular layer. It was found that ozone can oxidize Si surface quite actively even at room temperature due to the existence of atomic oxygen generated by the decomposition from ozone [25]. The properties of ozone oxidation are as bellow: (1) atomic oxygen directly attacks the back bond of Si; (2) it can oxidize H-terminated Si surface which oxygen molecule could not attack; (3) less suboxide interface by ozone, and (4) layer by layer growth occurs by ozone oxidation. The ozone oxidizes the passivated surface more rapidly than oxygen, and that ozone can oxidize the hydrogen passivated surface where oxygen molecules do not adsorb. Ozone oxidation is proceeded with atomic oxygen and molecular oxygen which are dissociated from ozone molecule. Three backbonds of a Si atom are changed to Si-O-Si bridge

simultaneously when ozone oxidation proceeds on the passivated surface [26].

The property of ultra-thin oxide by ozone water process attracts our attention to study. The main purpose of this method is to investigate the mechanism and the application of ultra-thin ozone oxide prior to high-k dielectric deposition. In this study, the characteristics of ozone oxide were established and the growth curves were also constructed in our experiments. Moreover, the roughness of ozone treated surface was measured by AFM analysis. The quality of ozone oxide was investigated by measurement of etching rate.

## 2.2 Experiment

4 inch P-type prime Si (100) wafers were prepared by Hydrofluoric acid dipping to remove native oxide. The ultra-thin silicon dioxide was grown on bare Si at room temperature in different ozone water concentration. Fig. 2-1 shows the experimental instruments of ozone water generator.

The ozone generator (AnserosPAP-2000) uses high electrical field to decompose oxygen molecular and compose ozone. Ozone mixed in DI water and then was introduced into the buffer tank. The water in the buffer tank was pumped to dissolve unit and ozone water was produced. The ozone water was introduced into the tank in the bench. The 4-inch H-terminal Si (100) wafer was immersed in the ozone water and silicon dioxide was formed on the Si. The thickness of oxide was measured by ellisometer, the relation between different ozone water concentration and thickness was studied.

The oxide growth rate depends on ozone water concentration. Ozone water concentration was controlled by water flow, oxygen flow, and power. Water flow must

be adjusted to keep the ozone concentration invariably. Ozone water concentration reduced from dissolve unit to the tank in the bench because of ozone decomposition during ozone water transportation.

## 2.3 Results and discussion

One of the potential characteristics of ozone oxide is to improve surface roughness. 6 inch P-type prime Si (100) wafers were prepared by Hydrofluoric acid dipping to remove native oxide. Fig. 2-2(a) shows the AFM measurement result of bare silicon. The Root Mean Square (RMS) value of the bare silicon is 0.123 nm. Then thin ozone oxide was grown on the silicon surface. As shows in Fig. 2-2(b), the Rms value of the ozone oxide surface is 0.111 nm. Finally, we dipped out the ozone oxide by HF and then measured it's surface roughness by AFM analysis. The results are showed in Fig. 2-2(c); the Rms value equals 0.071 nm. The Rms value decreases from 0.123 nm to 0.071nm. This means that the ozone oxide has the ability to improve the surface roughness.

Fig. 2-3(a) illustrates the Rms value of oxide growth by ozone water treatment is 0.115nm. Fig. 2-3(b) shows the Rms value of ozone oxide followed by rapid thermal process 800°C 30 seconds in N<sub>2</sub> ambient is 0.112nm. Fig 2-3(c) illustrates the Rms value of ozone oxide with RTP 800°C for 30 seconds followed by 800°C in NH<sub>3</sub> ambient furnace for 1 hour is 0.108nm. It is evidence that surface roughness of ozone oxide followed by nitridation process could be improved. Fig 2-3(d) shows the Rms value of ozone oxide followed by a 250 Å thick Al<sub>2</sub>O<sub>3</sub> film deposition is 0.193nm, the surface roughness of Al<sub>2</sub>O<sub>3</sub> is flat.

Fig. 2-4 shows the growth curves of the ultra-thin ozone oxide. The oxide

thickness is depending on the concentration of the ozone water. During the first 5 min, the higher concentrations of ozone water, the higher growth rate of ozone oxide. However, after 5 min, the oxide thickness seems to be saturated and independent of ozone water concentration. This shows that ozone oxide has a self-limit property during oxidation in ozone water.

Fig. 2-5 shows the etching rate of both ozone oxide and chemical oxide. We compared the etching rate of ozone oxide and the chemical oxide. Chemical oxide was prepared by RCA clean without HF-dip. The etching rate of the chemical oxide is from 2.09 Å/min to 4.16 Å/min. For ozone oxide, the initial etching rate is 2.66 Å/min and then down to 1.01 Å/min. This result demonstrates that the ozone oxide has higher density than chemical oxide.

## 2.4 Summary



In this study, it is demonstrated that the ozone oxide possessed the characteristics as below: dense film, high quality film near interface, self-limited growth, flat surface roughness. Ozone water treatment is a potential method for ultra-thin oxide growth.

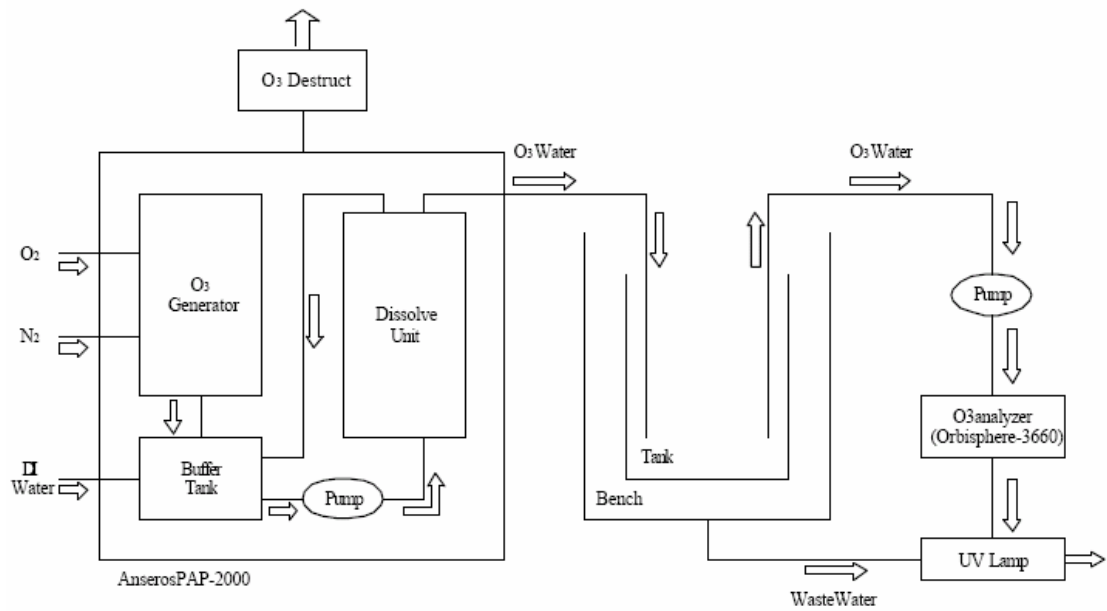
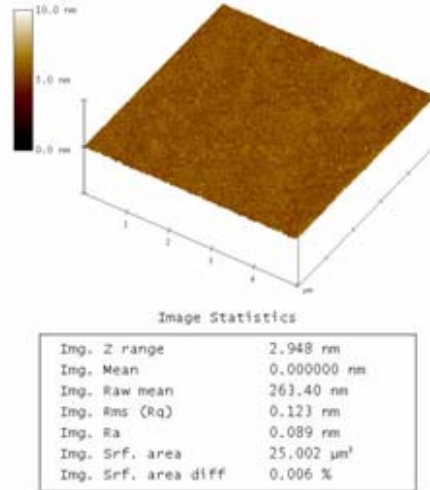


Fig. 2-1 The schematic illustration for measuring of ozone water system



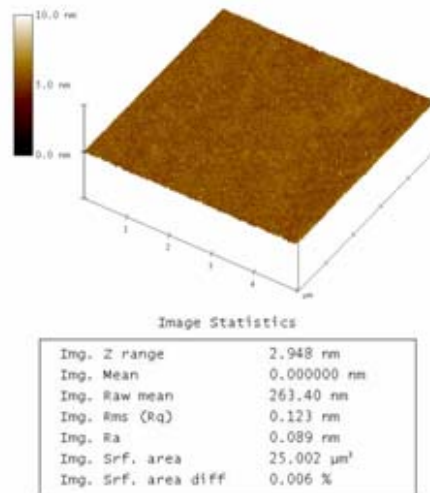
(a) Bare Si

Rms=0.123nm



(b) Ozone oxide

Rms=0.111nm



(c) HF-dip

Rms=0.071nm

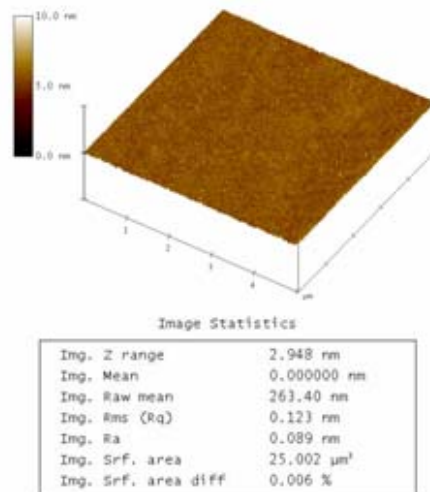


Fig. 2-2 AFM measurement results

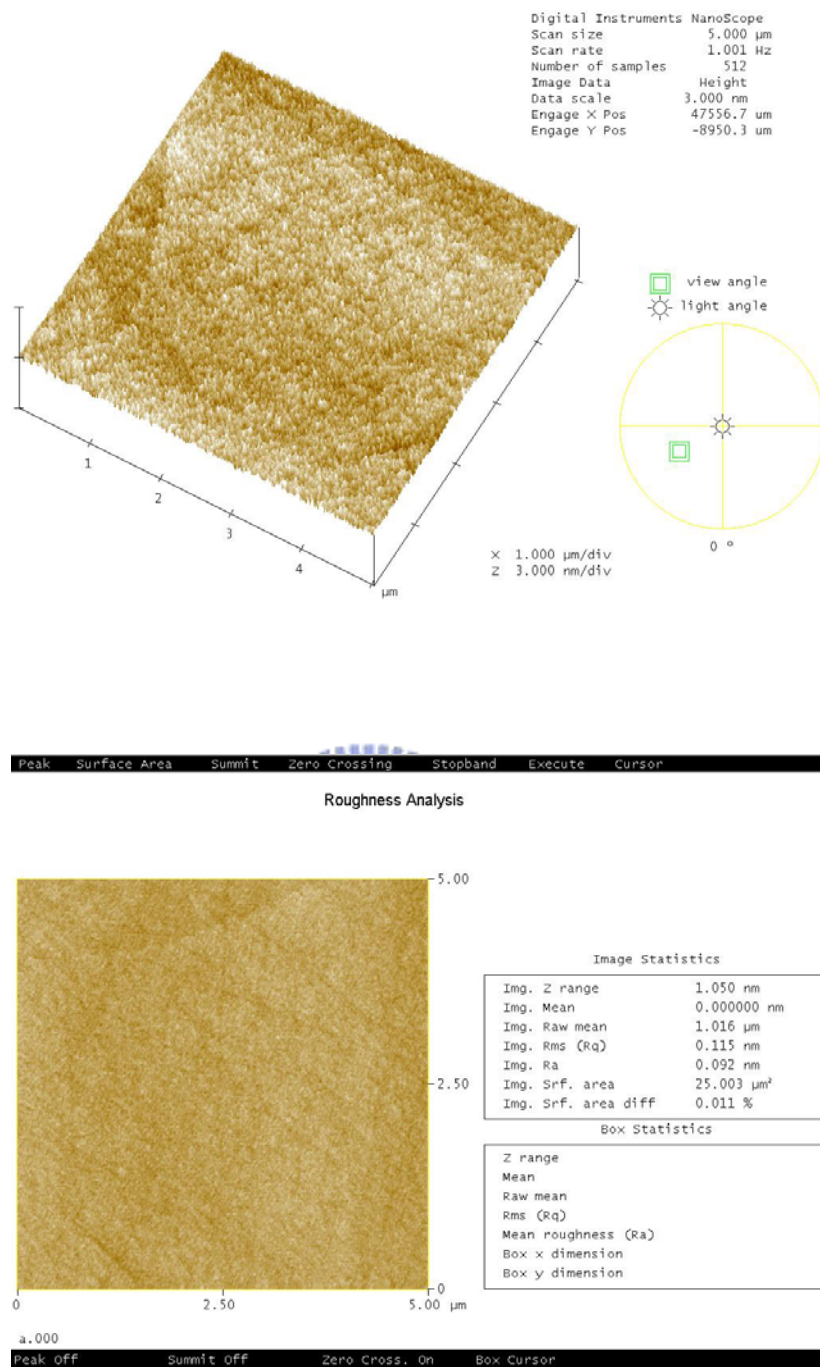


Fig. 2-3 (a) AFM result of oxide growth by ozone water treatment

→Rms=0.115nm

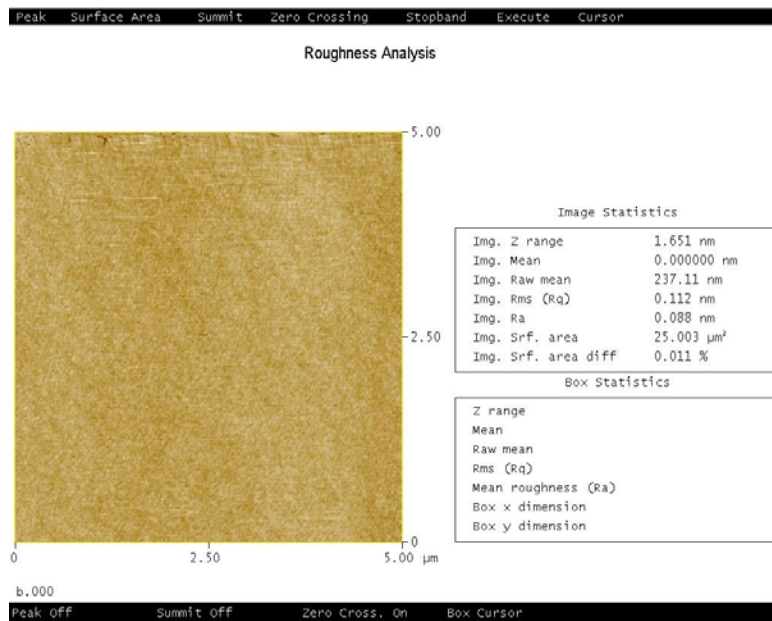
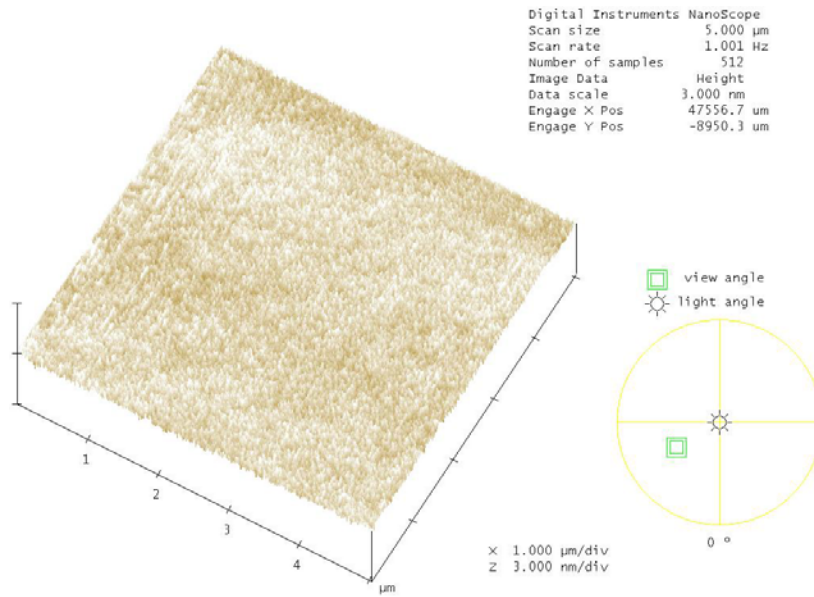


Fig. 2-3 (b) AFM result of oxide growth by ozone treatment followed by RTP at 800°C for 30 seconds  $\rightarrow$  Rms=0.112nm



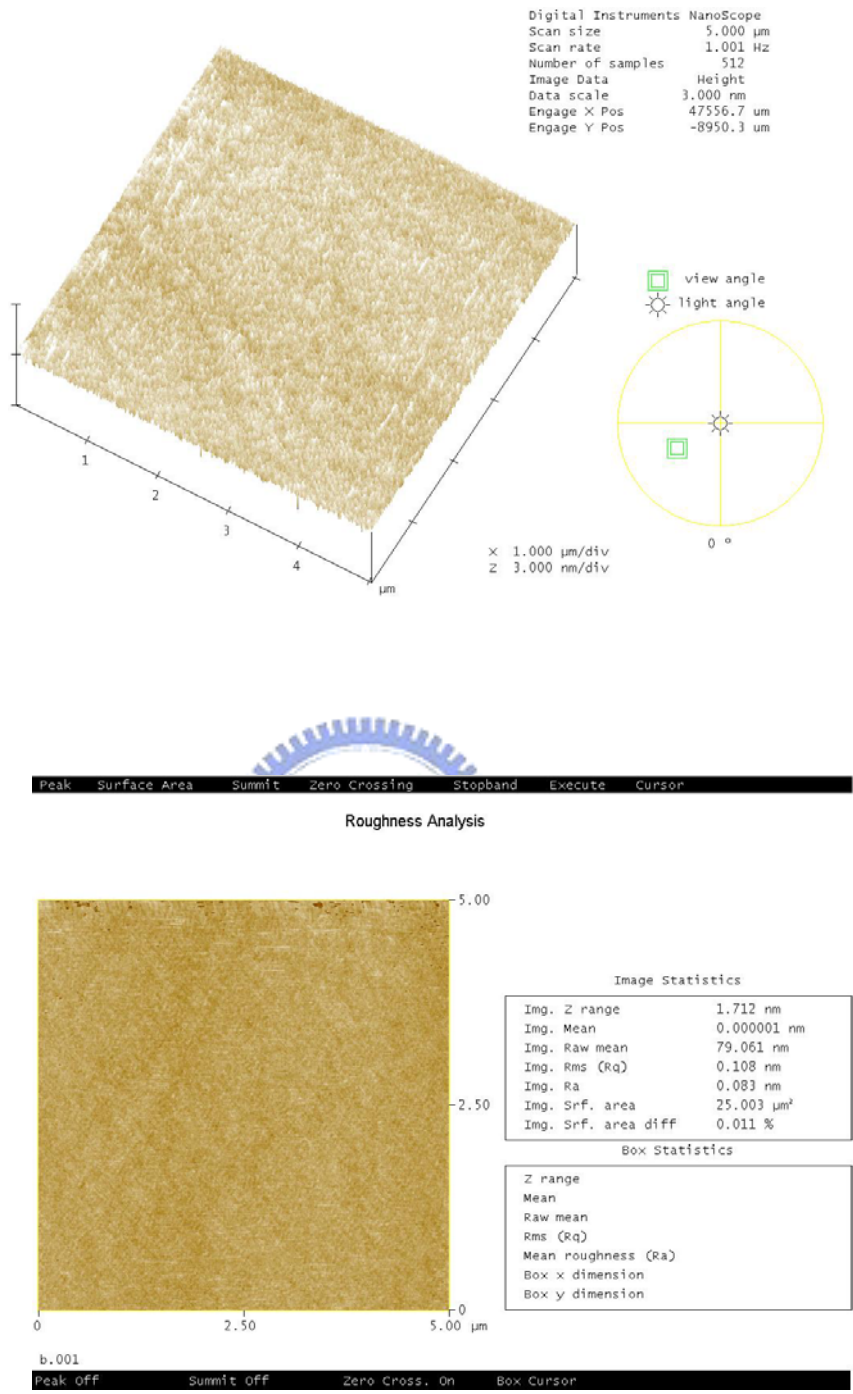


Fig. 2-3 (c) AFM result of oxide growth by ozone treatment with RTP  
 800°C 30sec followed by nitridation process → Rms=0.108nm

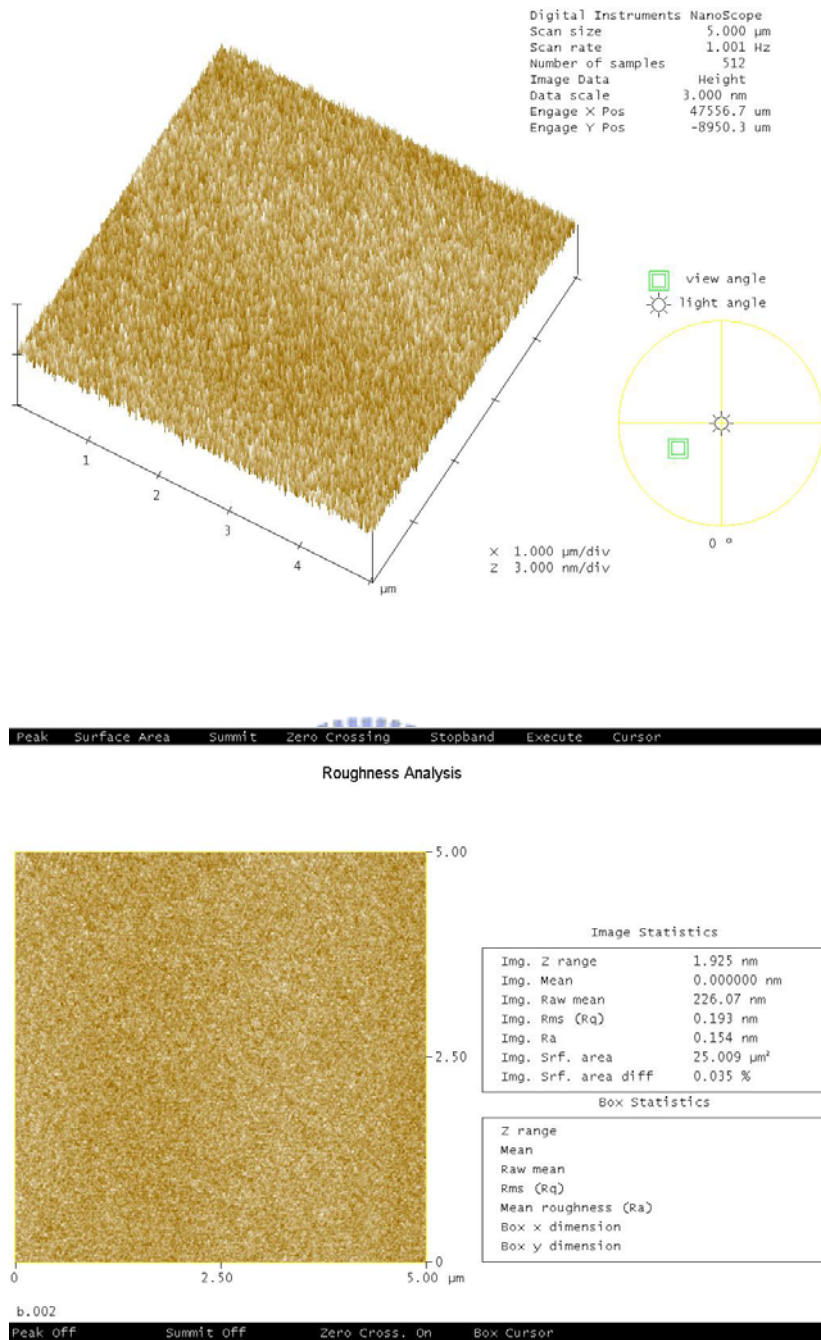


Fig. 2-3 (d) AFM result of oxide growth by ozone treatment followed by 250Å Al<sub>2</sub>O<sub>3</sub> film deposition → Rms=0.193nm

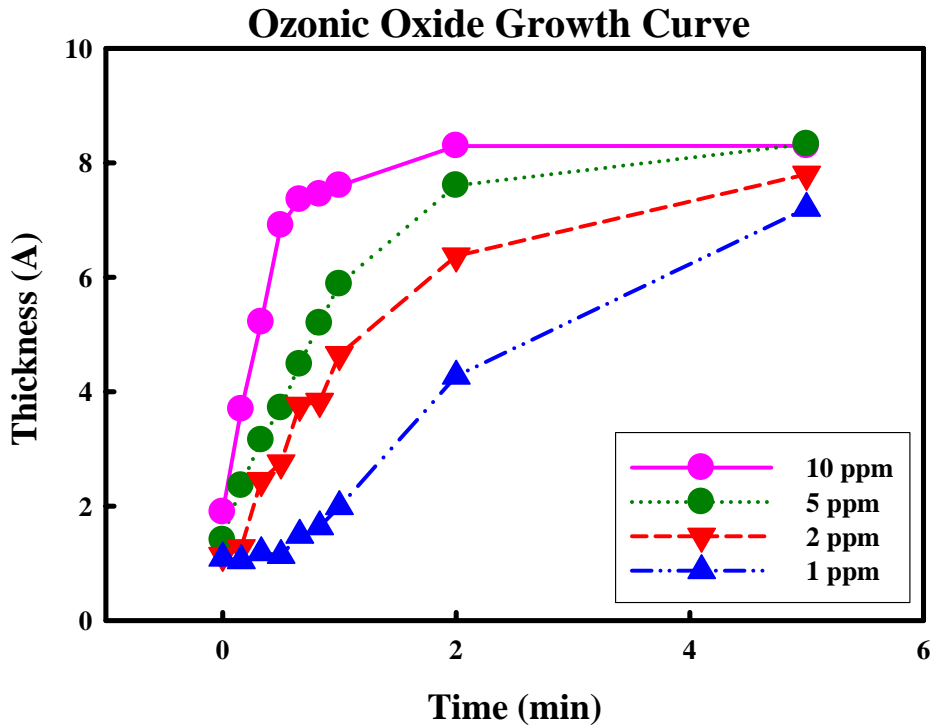


Fig. 2-4 The growth curves of the ultra-thin ozone oxide

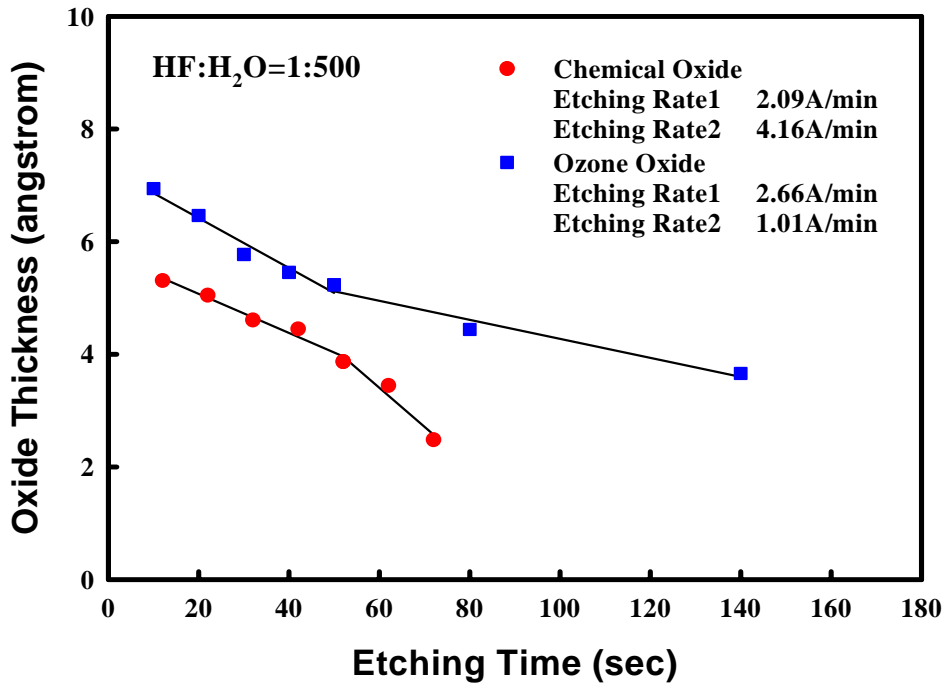


Fig. 2-5 The etching rate of both ozone oxide and chemical oxide