

Hafnium Nitrate Precursor Synthesis and HfO₂ Thin Film Deposition

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The paper will introduce a simple new method on the synthesis of both hafnium and zirconium nitrate precursors. The intermediate product, dinitrogen pentoxide produced from the water extraction from fume nitric acid via phosphorus pentoxide, was condensed by liquid nitrogen trap into a flask equipped with hafnium or zirconium tetrachloride. To give the high yield, the mixture of fume nitric acid and phosphorus pentoxide was heated to a certain temperature, from which large quantity of dinitrogen pentoxide had been generated. In the following step, hafnium or zirconium tetrachloride was refluxed over dinitrogen pentoxide at 30 to 35 °C for half-hour. The product was purified by sublimation. High yield, above 95%, was obtained. The cost for the hafnium nitrate precursor synthesis was estimated. The precursor was not stable at room temperature, and should be stored in refrigerator in sealed vials. No chlorine was detected from both EDS and chemical analysis. The volatility was evaluated by thermal gravity analysis. For high *k* thin film applications, the precursors were evaluated through the hafnium oxide thin film deposition via ALD process. High quality hafnium oxide thin films were obtained. The hafnium oxide thin film property consistence using different batches of our synthesized hafnium nitrate precursor was also verified. X-ray diffraction analysis indicated the films were smooth, uniform, amorphous as deposited and monoclinic after post annealing. For as-deposited hafnium oxide thin films, XPS studies showed the films were rich in oxygen and contained nitrogen residues,

which could be eliminated from forming gas post-annealing process. On the electrical property measurement, the 57Å hafnium oxide thin film showed a dielectric constant of $k \sim 10.5$ and a capacitive equivalent thickness of approximately 21Å.

Keywords: hafnium nitrate, ALD process, hafnium oxide thin film

INTRODUCTION

Recently, hafnium oxide thin film deposition via atomic layer chemical vapor deposition (ALCVD) process has been attracted great attention because of its high potential applications in semiconductor industry as high k gate oxide material. Precursors for hafnium oxide thin film deposition via ALCVD process have been evaluated and developed. Among those, hafnium tetrachloride, hafnium **b**-diketone, hafnium alkoxide and hafnium nitrate are mainly four compounds under consideration. However, the first three, comparing to hafnium nitrate, are not capable for the deposition of high quality hafnium oxide thin film via ALCVD process on hydrogen terminate silicon wafers. Hafnium tetrachloride can be used for hafnium oxide thin film ALCVD process on SiO_2 or Si_3N_4 substrate, but failed on hydrogen terminated Si wafers because of poor quality. Hafnium **b**-diketone, such as $\text{Hf}(\text{thd})_4$, gives high deposition temperature in CVD process, and in ALCVD process on SiO_2 substrate, gives rough hafnium oxide thin film and high carbon contamination. Hafnium alkoxide precursors are extremely sensitive to air and moisture, which results in not only the difficulty in handling, but fast decomposition in the cycle of water during the ALCVD

process. Hafnium nitrate is different. Firstly, it does not contain both carbon and hydrogen, and eliminates the possibility of both hydrogen and carbon contamination in the deposited hafnium oxide thin films. Secondly, it is not extremely sensitive to air, which leads to easy precursor handling operation. And finally, the most important is it gives high quality hafnium oxide thin film on hydrogen terminated silicon wafer via ALCVD process.

In this paper, we are going to describe a simple method for the synthesis of laboratory scale hafnium nitrate precursor, and also, the hafnium oxide thin film properties using this hafnium nitrate precursor will be introduced.

Hafnium Nitrate Precursor Synthesis

In the early of 1960's, the preparation of zirconium nitrate was reported by B.O. Field^[1] according to the reaction between zirconium tetrachloride and dinitrogen pentoxide, as shown in equation (1). The dinitrogen pentoxide can be obtained by the dehydration of fuming nitric acid over P₂O₅ according to the reaction of equation (2).



The product was obtained by refluxing ZrCl₄ in excess dinitrogen pentoxide at 30 °C for 30 minutes, and purified by sublimation. After the first sublimation, the compound was confirmed as the adduct of both N₂O₅ and N₂O₄, and then further purified as pure Zr(NO₃)₄ after the second

sublimation. However, since the non-stability of dinitrogen pentoxide even at low temperature, we can follow Field's synthesis procedure directly only until we can manage in-site preparation of dinitrogen pentoxide. The following is the description of our lab-scale zirconium or hafnium nitrate precursor synthesis method.

Figure 1 is the synthesis apparatus, and the Figure 2 describes the synthesis procedures for hafnium nitrate precursor, from which zirconium nitrate can also be prepared in high yield.

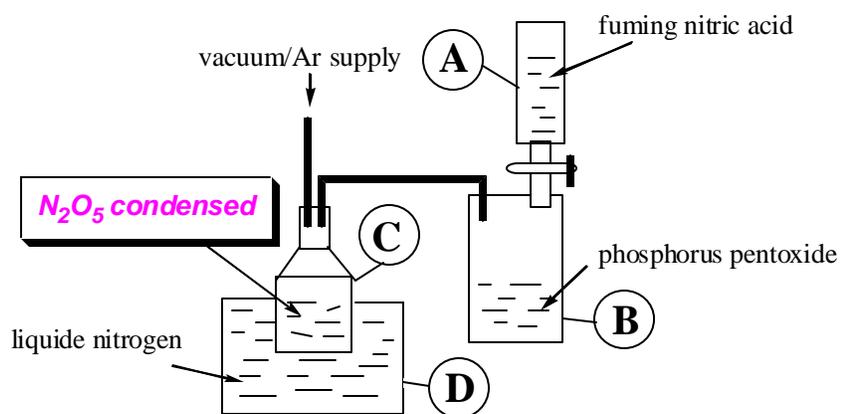


Figure 1. Apparatus for the synthesis of hafnium nitrate

Both phosphorus pentoxide and hafnium tetrachloride were equipped into flasks B and C in glove box, and then the system was installed in a manifold line. The fuming nitric acid was filled into a graduated cylinder, and then little vacuum was applied. Flask C was immersed into liquid nitrogen filled vessel D. Then the fuming nitric acid was slowly dropped into flask B. Dinitrogen pentoxide, formed from the dehydration of fuming nitric acid over phosphorus pentoxide, was condensed into flask

C as white crystals. It takes several hours for the dehydration process. When enough dinitrogen pentoxide was collected in flask C, a long distillation column was equipped on flask C, and then the flask C was heated to 32 °C in a water bath. At this temperature, hafnium tetrachloride was refluxed over dinitrogen pentoxide for 30 minutes. The refluxing liquid was in a deep yellow color. After reflux, the flask C was connected to a dynamic vacuum line, and the compound was stripped to dryness as white solid, which was then purified via sublimation to white crystals.

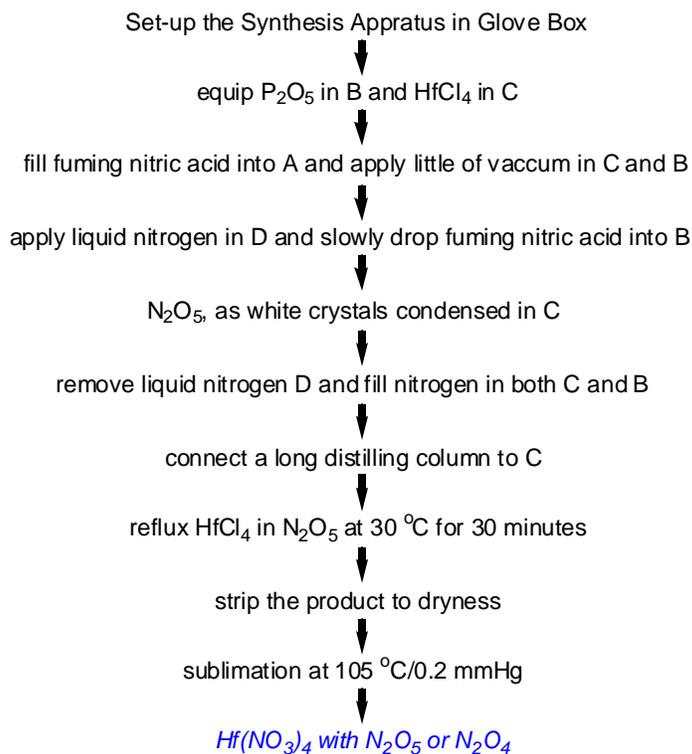


Figure 2. Procedures of the synthesis of hafnium nitrate

Chemical analysis indicates the white crystals consist of hafnium, oxygen and nitrogen. No chlorine was detected, which was consistent to

the EDS result as shown in Figure 3. Comparing to the calculated hafnium, oxygen and nitrogen composition in the formula of $\text{Hf}(\text{NO}_3)_4$, chemical analysis results give lower hafnium. Thus the white crystals, after the first sublimation, were believed to be the hafnium nitrate coordinated with nitrogen-oxygen compound.

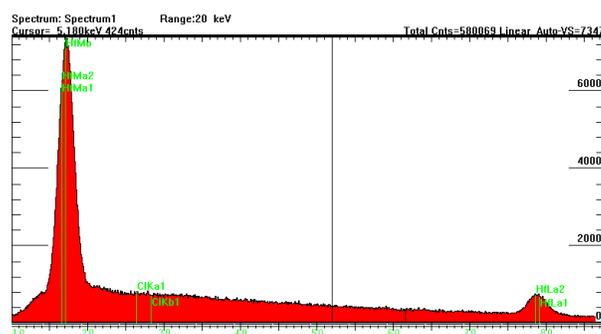
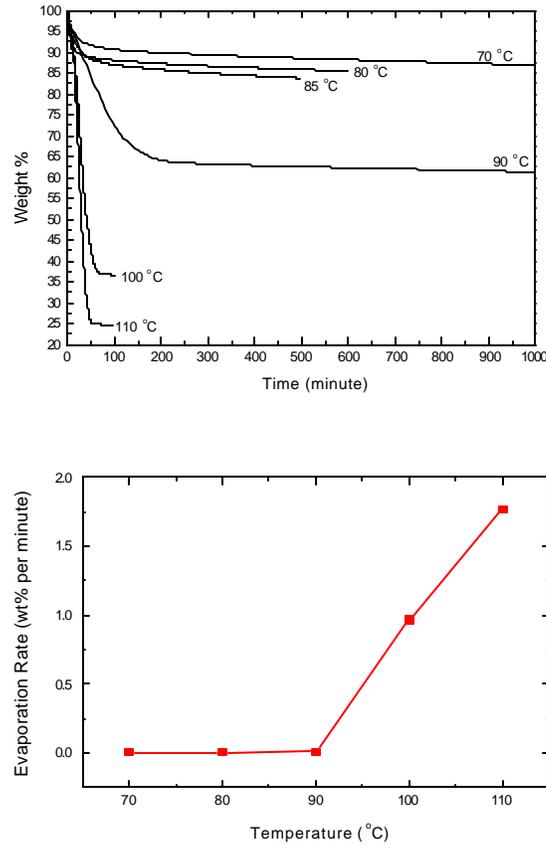


Figure 3. EDS of hafnium nitrate

Thermal Properties of hafnium nitrate precursor

The thermal properties of synthesized hafnium nitrate precursor were evaluated by TGA. In the TGA experiments, samples were heated to the designed temperature quickly, and then the weight loss was recorded when the temperature was balanced. The weight losses recorded were at balanced temperatures of 70, 80, 85, 90, 100 and 110 °C respectively, and the results were shown in Figure 4. When the hafnium nitrate precursors were heated from 70 to 85 °C, the weight losses at balanced temperatures were low, and so the constant precursor evaporation can be maintained over a long time. As temperature increases, the weight loss increases, and so the amount of precursor evaporated can not be maintained as a constant over a long time. According to TGA results, on the purpose of stable

hafnium oxide thin film deposition, the precursor heating temperature should be in the range of 80 to 85 °C.



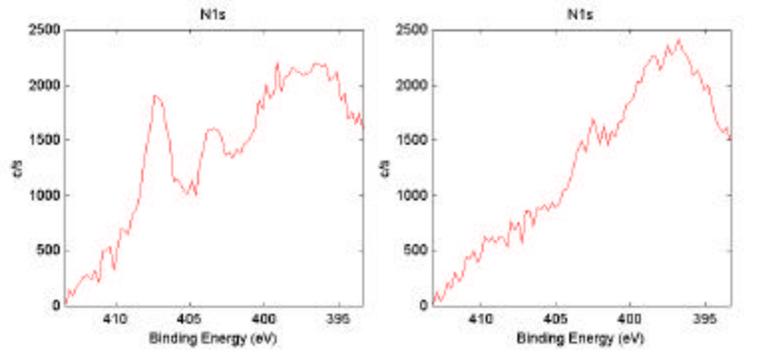
(a) weight loss vs heating time (b) weight loss vs temperature

Figure 4. TGA results at different temperatures

Hafnium oxide thin film properties using hafnium nitrate precursor

Hafnium oxide thin film was deposited directly onto hydrogen terminated Si via ALCVD. The temperature for the precursor delivery was 82 °C. The pulse sequence in each cycle is the first of 0.6s $\text{Hf}(\text{NO}_3)_4$, followed by 0.6s

N_2 and 0.6s water, and finally 0.6s N_2 . The deposition temperature was 180 °C, from which 0.36 nm/cycle deposition rate was obtained. XPS



(a) as-deposited (b) RTA at 450 °C for 30s under N_2

Figure 6. XPS studies on hafnium oxide thin film

studies indicated the as-deposited hafnium oxide thin films contained about 1.2% amount of nitrogen. However, after RTA process at 450 °C for 30 seconds in forming gas, the nitrogen was decreased to less than 0.2%, as shown in Figure 6. In XRD studies shown in Figure 7, the as-deposited hafnium oxide thin film has amorphous phase, and after RTA post-annealing at 850 °C for 300 seconds under nitrogen atmosphere, the thin film is in the monoclinic phase. The dielectric constant of $HfO_{2-stack}$ thin film is about 10.7, determined from C-V measurement as shown in Figure 8. The thickness of hafnium oxide thin film for the C-V measurement was 57 Å, and the size was about 200 nm.

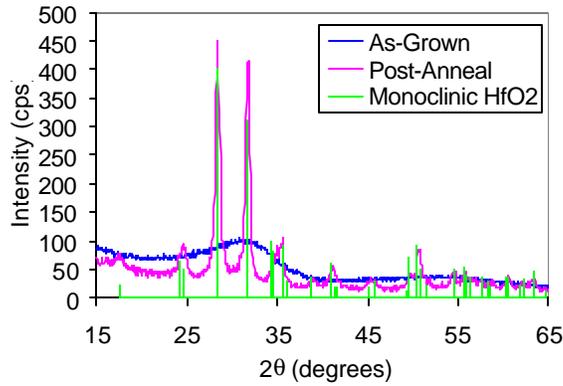


Figure 7. XRD spectra of hafnium oxide thin film

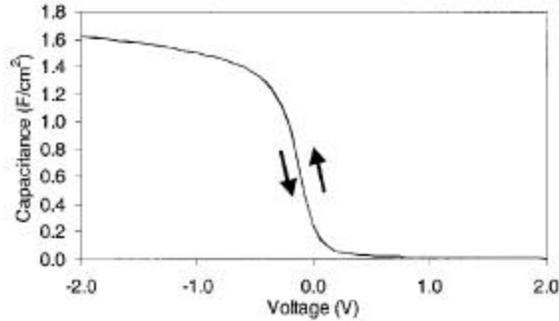


Figure 8. C-V curve for hafnium oxide thin film

Further experiments indicated the similar hafnium oxide thin film deposition rate using different batch of hafnium nitrate precursors. The improvement of electric properties is still going on.

Summary

A simple method for the synthesis of lab-scale hafnium nitrate precursor has been presented. Detailed thermal property studies indicate the precursor has stable mass delivery property in the temperatures ranging from 70 to 85 °C, which leads stable and repeatable hafnium oxide thin film deposition via ALCVD process. The hafnium oxide thin film showed monoclinic phase

after RTA process, and has the dielectric constant about 10.7 for 57 Å thick HfO_{2-stack} thin film.

References

- [1] B.R. Field and C.J. Hardy, Proc. Chem. Soc. 76-77 (1962)