

Evaluation of tetrakis(diethylamino)hafnium Precursor in the Formation of Hafnium Oxide Films Using Atomic Layer Deposition

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ABSTRACT

Due to their compatibility with silicon interface and high dielectric constant, films containing hafnium oxide are becoming strong candidates in replacing silicon oxynitride as the gate dielectric layer in CMOS devices. To achieve ultimate conformality and thickness control, atomic layer deposition is receiving much more attention in recent years for nanometer size film applications. For hafnium oxide deposition by ALD, metal chlorides have traditionally been used as precursors with moisture being the co-reactant; however for gate oxide applications, metal chlorides are not considered suitable due to the corrosive nature of these compounds and the risks of film contamination. Hence, researchers are exploring alternate organometallic precursors in a CVD process with oxygen being the co-reactant. In this work, tetrakis (diethylamino) hafnium precursor is used in an ALD process with moisture co-reactant to deposit hafnium oxide films onto H-terminated Si substrate in a temperature regime of 200 to 350 C. Film composition is determined by x-ray analysis and is found to be stoichiometric without residue from ligand decomposition. Film thickness and uniformity is measured as a function of substrate temperature and reagent pulsing characteristics. These results will be presented and compared with that obtained with the more conventional hafnium chloride precursor.

INTRODUCTION

As semiconductor design features shrink to sub-100 nm dimension, new materials are needed in order to meet more stringent performance demands. One of the greatest technical challenges today in semiconductor manufacturing is the implementation of new high dielectric materials needed for the gate oxide insulator in CMOS transistors [1]. In recent years, several metal oxides such as HfO_2 , ZrO_2 , Al_2O_3 along with their silicate and aluminate analogs have been studied as potential candidates.[2-7] Among these different metal oxides, hafnium oxide has received much attention due to its higher resistance and dielectric constant [8,9] and its thermal stability on silicon.[10,11]

Thin film deposition of metal oxides such as HfO_2 has been achieved by oxidative and hydrolytic reactions with various hafnium precursors both by chemical vapor deposition (CVD) and by atomic layer deposition (ALD). Deposition by oxidation has been done by chemical vapor deposition using tetrakis (diethylamino) hafnium precursor ($\text{Hf}(\text{DEA})_4$) and oxygen at relatively high temperatures of 300- 425 C. [12-14] Although good step coverage was obtained, there was typically a few percent of carbon and nitrogen in the film.

The majority of thin film HfO_2 depositions however were done using hydrolysis of HfCl_4 [15-17] and the chemical stability of the resulting films with Si substrate has been studied.

[18,19] The reaction of HfCl_4 with H_2O is very fast. To take advantage of such chemistry, the reactants are introduced into the reactor in an alternating pulse-purge injection mode known as atomic layer deposition (ALD). ALD produced stoichiometric HfO_2 films from 180 to 940 C. The growth rate decreased from ~ 3 to 0.8 Angstroms per cycle as the temperature increased in this range and the phase properties of the films depended on substrate temperature and thickness.

Alternatively, the ALD technique can be applied to the hydrolysis of alkylamino-hafnium precursors. In fact tetrakis (ethylmethylamino) hafnium ($\text{Hf}(\text{EMA})_4$) has recently been demonstrated. [20] Despite the bulky organic ligands, the residual carbon and nitrogen in the film was much less than that observed in films obtained by CVD using $\text{Hf}(\text{DEA})_4$ [12-14]. And unlike the HfCl_4 studies, the growth rate increases from ~ 1 to 1.5 Angstrom per cycle as temperature increases 250 to 350 C. In this study, atomic layer deposition of HfO_2 films on native-oxide free silicon was performed using $\text{Hf}(\text{DEA})_4$ precursor with H_2O being the co-reactant in order to evaluate this precursor in an ALD process and to compare results with the corresponding chloride precursor HfCl_4 .

EXPERIMENTAL DESCRIPTION

Hafnium oxide films have been deposited onto silicon substrates using a hot wall quartz tube reactor with an alternating-pulse reagent introduction manifold. In this reactor the temperature can be maintained between ambient and 650°C using a thermostatically controlled resistive heating coil situated outside the reactor wall. The reagent manifold allows for fast pulsing and purging of either reagent stream into the reactor.

In order to perform atomic layer deposition, the reagents need to be sequentially pulsed with sufficient purge times in between reagent pulses to allow all the remaining vapor phase and multiple-layer adsorbed species to be removed from the substrate prior to introduction of the next reagent pulse. In this study a computer controls pneumatic actuating valves and defines the pulse/purge sequence. The hafnium precursor pulse varies from 1 to 15 seconds in length while the moisture pulse is typically less than 1 second.

The precursor stream originates by flowing ~ 100 sccm of Argon carrier gas over a quartz open-boat type reservoir containing the precursor. The precursor reservoir, which can accommodate either solid or liquid chemical, is situated in a thermostated stainless steel vessel. In these studies, the $\text{Hf}(\text{DEA})_4$ and HfCl_4 were maintained at 80° and 140° C respectively.

In these experiments, the moisture originates from an isothermal reservoir containing a few milliliters of pure H_2O at liquid-vapor equilibrium conditions (~ 1.7 Torr at 25°C). The pressure drop between the moisture vessel and the manifold insures the flow of moisture into the chamber during the pulse-on step. Typically, 100 to 300 cycles were used to obtain films of varying thickness. The resulting films were then characterized by reflectometry (Mission Peak Optics model MP100-S), energy dispersive x-ray (EDX) spectroscopy (Amray Model 1600), and ellipsometry (J. A. Woollam Model 200 M) .

PRECURSOR PROPERTIES

The information on the properties of these precursors is limited in the literature so additional measurements were done by differential scanning calorimeter and thermal gravimetric analysis. By calorimetry, the HfCl_4 was observed to sublime under ambient pressure conditions at 340 C prior to reaching any melting transition. The sublimation vapor pressure is estimated to

be ~0.5 Torr at 150 C based on this sublimation calorimeter data and higher temperature vapor pressure data in the literature^{21,22}. Calorimeter data on Hf(DEA)₄ indicates the compound decomposes at ~ 250 C prior to any evaporation transition so its boiling point can not be determined by this method.

To better assess relative volatility of the two precursors, thermal gravimetric analysis data indicates Hf(DEA)₄ to exhibit more volatility at lower temperatures; however, at higher temperatures a slight non volatile residue (~1-2%) results suggesting some thermal decomposition is occurring prior to complete vaporization.

Both limited literature data on the vapor pressure of these precursors and the thermal measurements done here indicate Hf(DEA)₄ to be the more volatile precursor. It also has the advantage of being a liquid at ambient temperatures; however, it is thermally less stable.

RESULTS

Rate of Film Deposition

The hafnium oxide films are deposited onto heated silicon substrates by repetitive pulse cycling of the hafnium precursor and moisture reagents. The resulting film thickness is observed to be linear with number of reagent pulse cycles for both hafnium precursors in the range of 150 to 500 cycles. However, in the case of the HfCl₄ precursor, the data indicates a negative y-intercept. This observation has been reported before in other ALD studies and is attributed to an initial exponential growth mechanism of the film that occurs on a primarily oxide-free silicon surface.[23]

In this mechanism the reactive sites for the initial deposition are limited but increase with number of repetitive cycles. After a certain number of cycles, the reactive sites cover the entire surface and remain constant and at this point linear growth is observed.[24] In this case, it takes ~50 cycles until reactive sites fully cover the surface and linear growth is observed.

Once linear film growth is established, the mechanism of atomic layer deposition can be confirmed by examining the growth rate dependence on precursor pulse duration. Figure 1(a) summarizes the data obtained while varying precursor pulse duration and keeping all other deposition conditions the same.

The figure shows similar dependence for both precursors. This result is not too surprising in view of the mechanism involved with atomic layer deposition. At around 4 - 5 second pulse duration, the growth rate appears to reach a plateau, and all the reactive surface sites are fully adsorbed with each pulse. At this point further lengthening of the precursor pulse does not increase growth rate as the surface becomes fully saturated and deposition rate becomes surface site limited instead of precursor reagent limited. At this limit, the growth rate is around 1.4 Å/cycle. To saturate the surface in a shorter time, the precursor source temperature can be increased; however, with the Hf(DEA)₄ precursor thermal degradation limits the source temperature to be under ~ 180 C.

In the case of Hf(DEA)₄ it is not certain whether such an exponential growth is occurring or not; more data is needed to confirm this point. If the growth is linear from the onset of deposition then the adsorption bonding of the Hf(DEA)₄ precursor onto silicon is substantially different from that of HfCl₄.

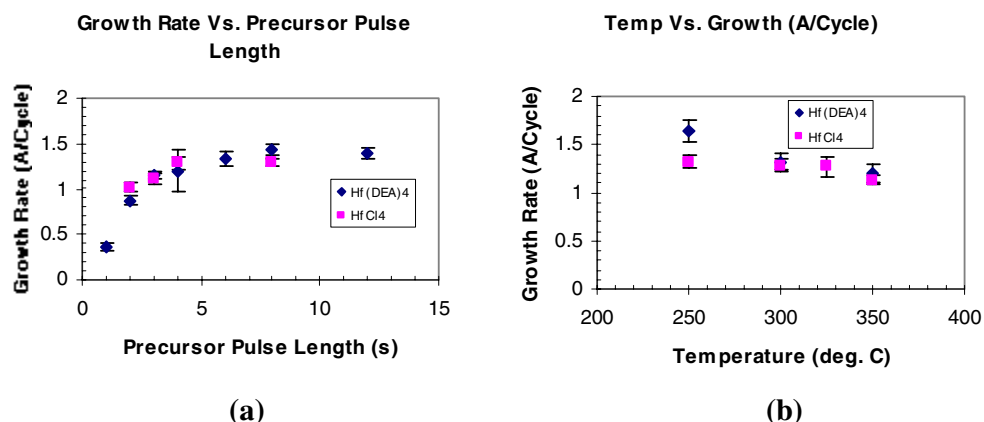


Fig 1. (a) Growth rate as a function of precursor pulse length at 300 deg C
(b) Growth rate as a function of temperature at 4 s precursor pulse length

Figure 1(b) shows that increasing substrate temperature decreases the growth rate (Å/Cycle) in the temperature range (250-350 C). Previous studies on effect of substrate temperature on ALD of HfO₂ by HfCl₄ show similar decrease in growth rate with increase in temperature.[15-19] Films grown using Hf(DEA)₄ show stronger but similar dependence of temperature on growth rate in our study. This can be due to adsorption characteristics of Hf(DEA)₄ on Si. The ALD study using Hf(EMA)₄ reports increase in growth rate with the increase in temperature for the same temperature window. They sight decomposition at higher temperature as the reason for this behavior. The fact that Hf(DEA)₄ is more stable than Hf(EMA)₄ might be the reason that we see similar temperature dependence as in the case of HfCl₄.

Given that the same substrate is used for both precursors and that the same substrate temperature is used, the film growth kinetics then becomes governed by number of available surface sites. Both precursors react sufficiently fast with the surface so as to not influence the kinetics and as a result the identity of hafnium precursor does not affect the film kinetics.

Deposition Film Properties

In this work, uniformity of the films were determined by two dimensional stepwise scanning measurements with the optical reflectometer keeping optical constants fixed at optimal values. The degree of uniformity depended more on reactor design than what precursor was used.

For each sample, 6 x 6 array spot analysis was performed over the full substrate dimension and the reported values represent averages of typically 3 such analyses. Since the analyses generally extends ~ a micron below the film surface, relatively thick film samples ~0.5 micron were prepared for this analyses. Samples generated from growth kinetics studies were also analyzed and, for the exception of increase silicon from the underlying substrate, no discernable differences were noted. In addition to Hf and O, suspected elements originating from potential ligand residuals (C, N, Cl) were also examined. Table 1 summarizes the relative abundance of elements in the films in weight percent.

Typical detection limit of Cl, and N is around 0.1 weight percent. The detection limit of C is somewhat higher ~ 0.2 %. The large excess of Si observed results from the depth volume of the EDX instrument extending beyond the film thickness and penetrating into the silicon substrate. Similar analysis of pre-cleaned silicon

Table I : HfO₂ Film Composition Analysis by EDX Analysis

Element	Analysis of Film Using HfCl₄ (atom percent)	Analysis of Film Using Hf(DEA)₄ (atom percent)
Hf	9.03	9.2
O	19.2	19.2
Si	71.34	71.0
C	< 0.4	< 0.6
Cl	N/D	N/D
N	N/D	N/D
O / Hf Ratio	2.12 +/- 35%	2.08 +/- 10%

substrates with no film deposited show only silicon with no detectable amounts of oxygen. Therefore, all oxygen observed by EDX results from that contained in the film itself. The only contaminant element observed is carbon. In the HfCl₄ generated film, the carbon is observed near the detectable limit and is attributed to handling issues; in the Hf(DEA)₄ generated film, marginally higher carbon level is observed.

The O:Hf mole ratio is the same for both precursors and indicates formation of HfO₂. If there was a large amount of hydrogen incorporation in the film (either as residual adsorbed H₂O or terminal hydroxyl groups), the ratio would be greater than 2.0. To the accuracy of the EDX analyses, the films do not show any substantial deviation from stoichiometric HfO₂.

CONCLUSION:

Sub-micron HfO₂ films have been deposited onto HF-cleaned silicon substrates using the atomic layer deposition technique with Hf(DEA)₄ precursor reacting with moisture. Comparison with the more standard HfCl₄ precursor shows many similarities in the resulting films. Under conditions studied, the growth rates appear identical and have same dependence on precursor pulse duration and number of cycles. At the substrate temperature of 300 C, elemental analyses of the films indicate no detectable chloride from HfCl₄ and no detectable nitrogen from the amino ligands of Hf(DEA)₄. This confirms the hydrolysis reaction of surface adsorbed Hf(DEA)₄ to be strongly bond selective to the metal – nitrogen bond; thus leaving a well intact alkyl amine as a gaseous by-product.

Under the experimental conditions used here, both precursors are suitable for ALD technique and both can generate very similar films. From the film properties examined here, the main difference in the two precursors is not so much in the film itself but in delivery considerations. The HfCl₄ is a solid in pure form and requires higher vaporization temperature than the Hf(DEA)₄ which is a liquid which can decompose at lower temperatures.

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