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Optimization of Plasma Enhanced Atomic Layer Deposition Processes for Oxides, Nitrides and Metals in the Oxford Instruments FlexAL™ reactor

C.J. Hodson¹, N. Singh¹, S.B.S. Heil², J.L. van Hemmen², W.M.M. Kessels²

¹Oxford Instruments Plasma Technology, North End, Yatton, BS49 4AP, United Kingdom

²Department of Applied Physics, Eindhoven University of Technology
PO Box 513 5600MB Eindhoven, The Netherlands

Hafnium oxide films deposited on silicon wafers from TEMA_H and O₂ plasma showed saturation at growth rate per cycle of 1.1 Å, which was independent of the plasma conditions. The same film deposited thermally using H₂O as the oxidant saturated at 0.8 Å/cycle. By varying the plasma exposure time the compositional ratio of [O]/[Hf], as calculated from RBS measurements, changed from 2.0 to 2.13. The carbon content in plasma HfO₂ films was < 2% compared to 8% in thermal HfO₂ films.

Titanium nitride films deposited on silicon wafers from TiCl₄ and N₂ / H₂ plasma showed saturation at 0.33 Å/cycle, which was independent of plasma conditions and a resistivity of <170 μΩ cm at 350°C deposition temperature. The stoichiometry of the films can be changed from being slightly nitrogen rich to titanium rich by varying the N:H ratios in the plasma and limiting the amount of nitrogen available for the reaction. The chlorine impurity in TiN varied according to plasma exposure time (2.6% to 1.2%) and N₂:H₂ gas ratio in the plasma, with a corresponding change in resistivity (200 μΩ - 150 μΩ).

Introduction

Plasma enhanced ALD is seen as a key enabling technology of ALD. By using plasma it is possible to deposit at lower temperatures, achieve better quality of films with lower impurities, deposit a wider range of materials with more choices of precursors, and control the properties of these materials by variation of the plasma conditions. This work reports the optimization of these plasma conditions to control and improve the film properties. References are made to thermal ALD films deposited in the Oxford Instruments FlexAL™ reactor for comparison to plasma processes.

The FlexAL™ reactor employs a remote plasma source that generates plasma species remotely from the substrate, preventing severe ion bombardment and therefore the plasma damage that has been reported for direct plasma ALD (2, 3).

In this study the deposition of HfO_2 and TiN in the Oxford Instruments FlexAL™ reactor by remote plasma ALD will be reported. HfO_2 is a high-k dielectric with many applications including gate dielectrics in DRAM transistors. TiN has applications as a barrier layer, for example to prevent Cu diffusion in back end of line CMOS processing and is used generally as a hard coating conductive coating, e.g. in the MEMS industry.

Experimental details

ALD reactor

Figure 1 shows a schematic which labels the key aspects of the FlexAL™ reactor. The system is loadlocked and can handle substrates up to 7mm in height/thickness and sizes from small wafer pieces up to 200mm wafers. Multiple precursor delivery modules housing the bubblers are located either side of the system with the shortest possible pipe length. The reactor has a remote plasma source situated above the substrate holder. Plasma gases are injected into the top of the source and precursors below the plasma source isolation valve. All areas of the system are heated and have independent computer control. The system is equipped with a variety of ports, for example in-situ spectroscopic ellipsometry and mass spectrometry.

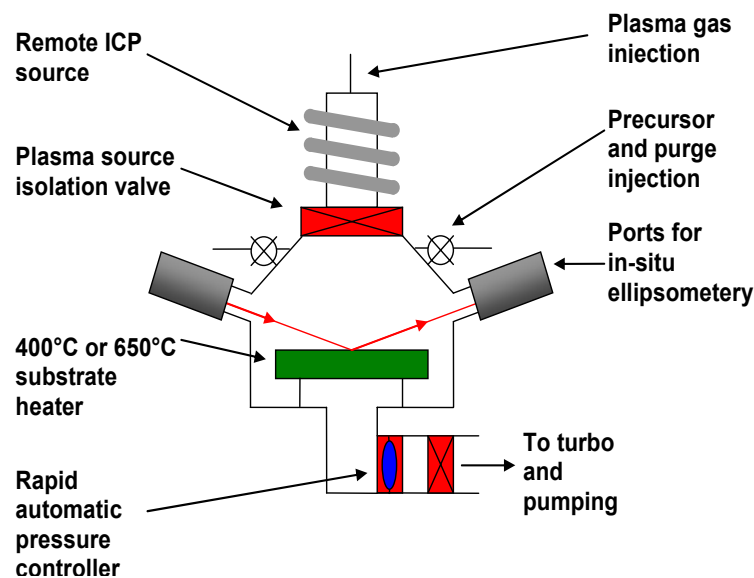


Figure 1 Schematic of the Oxford Instruments FlexAL™ reactor

Film synthesis

HfO_2 was grown using tetrakis(ethylmethylamino)hafnium or TEMAH which was bubbled with argon and heated to 70°C. The oxidant was either a remote O_2 plasma or water. The temperature of the wafer stage was varied from 230°C to 350°C (~ 200°C to 320°C wafer temperature) and the oxygen plasma exposure time was varied from 2 to 20

seconds. The effect of these deposition condition changes is reported in this paper. TiN was grown using titanium tetrachloride (TiCl_4) and a mixture of nitrogen and hydrogen as the plasma gases. The TiCl_4 has a high vapour pressure (9.6 Torr at 20°C) and so was controlled to above ambient temperature and no bubbling was required. The ratio of the nitrogen to hydrogen in the plasma was varied to examine the impact on film qualities. The wafer holder temperature was kept constant at 350°C ($\sim 320^\circ\text{C}$ wafer temperature).

The plasma pressure was controlled to 10mTorr which was found to be optimum for the remote plasma ALD source.

Film characterization

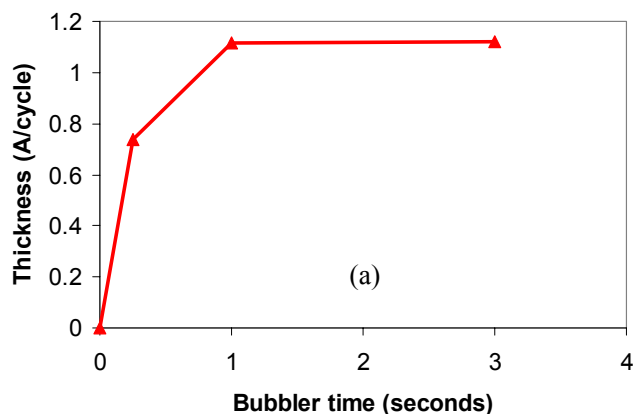
The thickness of the films was determined using a Nanospec 3000 (normal incidence reflectometer) from Nanometrics and a spectroscopic ellipsometer, the M2000D from J.A. Woollam.

The film composition was determined by Rutherford backscattering spectrometry (RBS) for Hf, O, C and Cl content. Elastic recoil detection (ERD) was used for determining the H content. A 2 MeV $^4\text{He}^+$ beam was used in these measurements. Film impurities were measured using Auger electron spectroscopy (AES). Argon was used to sputter through the film for depth profiling.

Results and discussion

Growth rate per cycle and saturation

Figure 2 shows the saturation curves for the HfO_2 . Films deposited on silicon wafers from TEMAH and O_2 plasma showed saturation at $1.1 \text{ \AA}/\text{cycle}$ and excellent thickness uniformity of $\pm 1.4\%$ across a 200mm wafer, which was independent of the plasma conditions. The same film deposited thermally using H_2O as the oxidant saturated at $0.8 \text{ \AA}/\text{cycle}$. In order to dose a small enough amount of water to achieve less than saturation a flow restrictor was used in series with the fast pulse valve. The pressure rise of each water dose into a sealed vessel was measured in a separate experiment and used to plot the x-axis in figure 2(d). The pressure rise of such a small dose of water is very difficult to measure accurately, hence the large error bars.



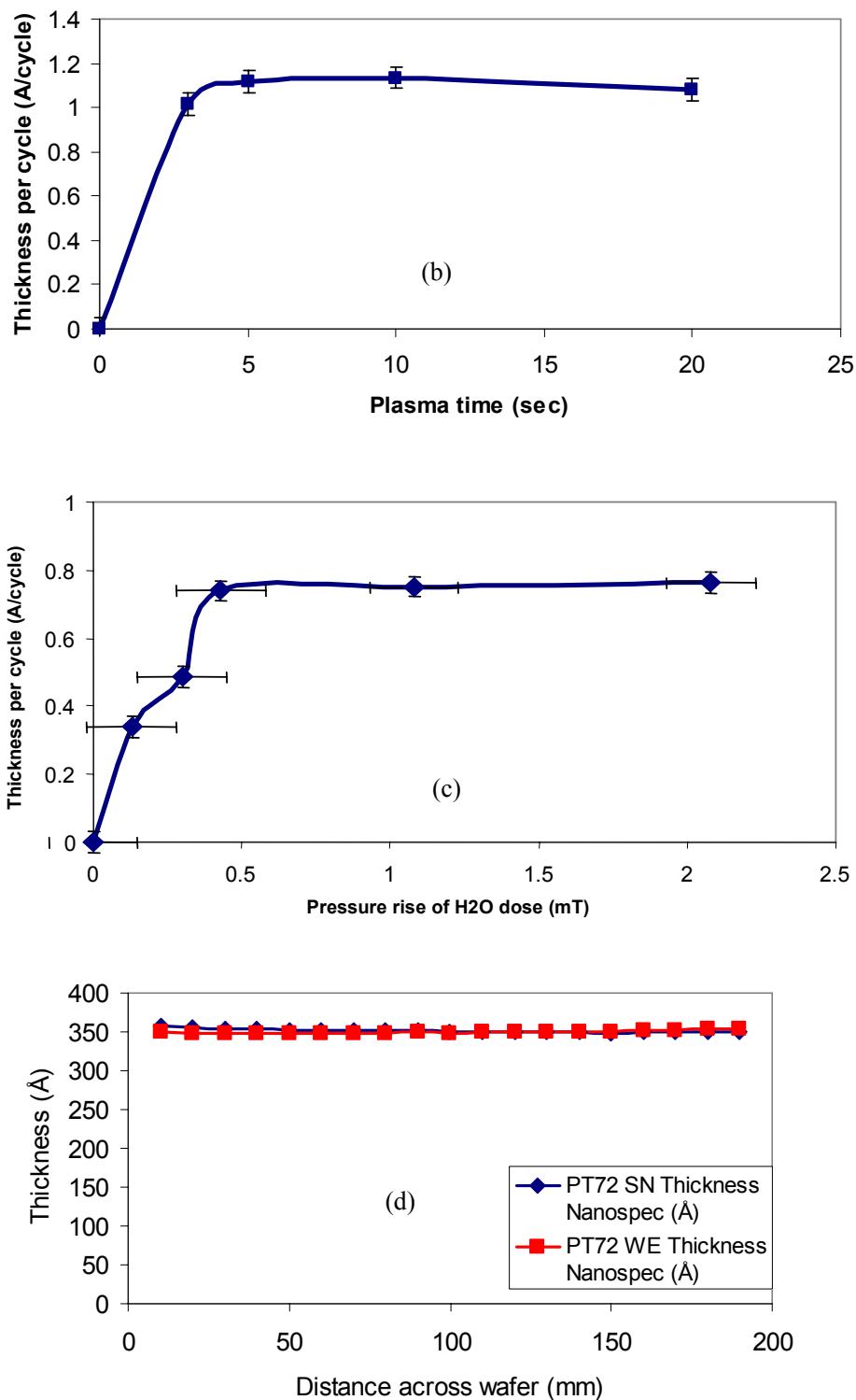


Figure 2 Saturation curves for HfO₂ using (a) TEMAH, (b) O₂ plasma and (c) H₂O. (d) Thickness uniformity of plasma HfO₂ less than $\pm 2\%$ for a 200mm wafer.

Figure 3 shows the characteristic linear growth for the TiN. The growth rate per cycle is saturated almost immediately with respect to the nitrogen/hydrogen plasma exposure time. It was also found that the plasma conditions had little or no impact on this growth rate per cycle.

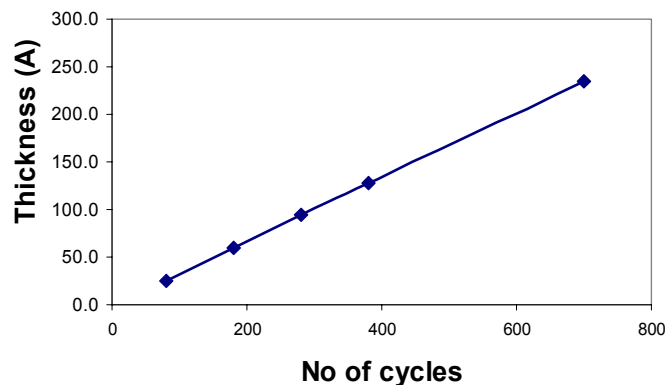


Figure 3 Linear growth of TiN on silicon with a thin native oxide shows almost no nucleation delay.

Composition and other properties

The effects of varying the plasma exposure time can be seen in figure 4. A compositional ratio of [O]/[Hf] 2.0 – 2.13 was obtained using RBS. The carbon and hydrogen impurities in the film are reduced with more prolonged plasma exposure. The detection limit of the RBS with respect to carbon is approximately 1-2%, hence the large error bars shown on the graph. For plasma exposure times greater than a few seconds it can be said the carbon content is less than 2%.

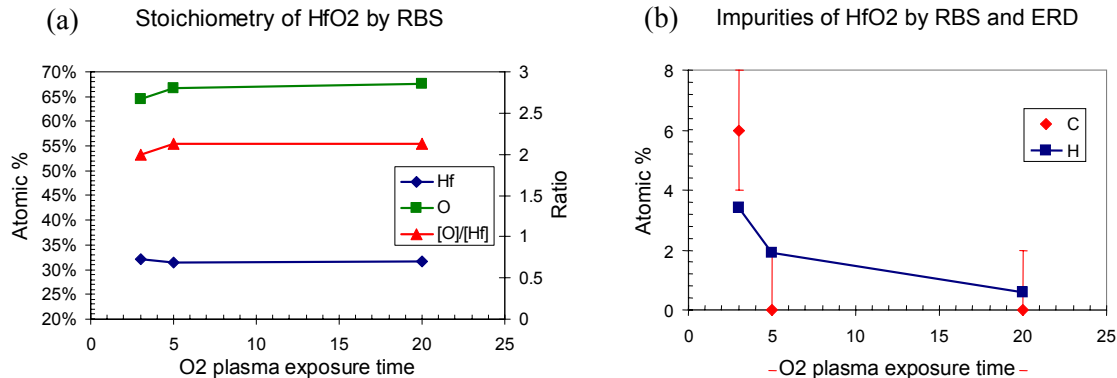


Figure 4 (a) Composition measured by RBS versus O₂ plasma exposure time (seconds), (b) Impurities measured by RBS (carbon) and ERD (hydrogen).

Figure 5 shows the effect of varying the deposition temperature. The hydrogen content in the film rises significantly. This series was for a 2 second plasma exposure. Further work is ongoing looking into improving the plasma conditions to reduce the deposition temperature window, which is important for several applications.

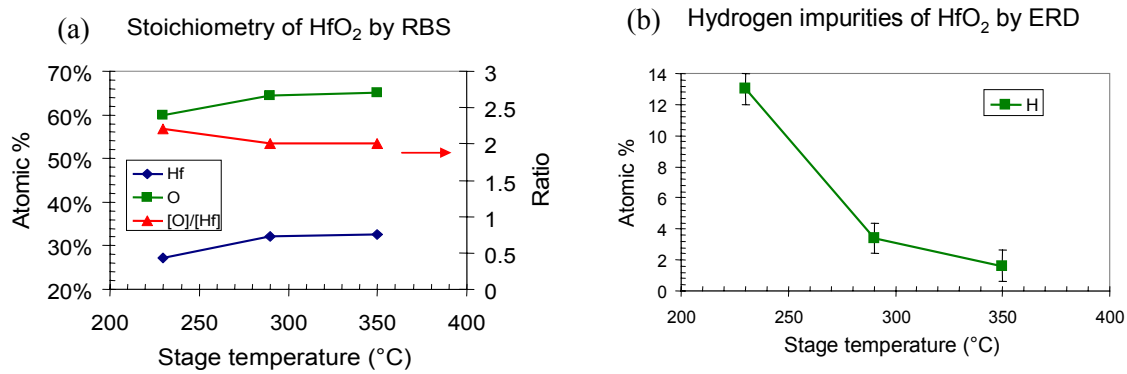
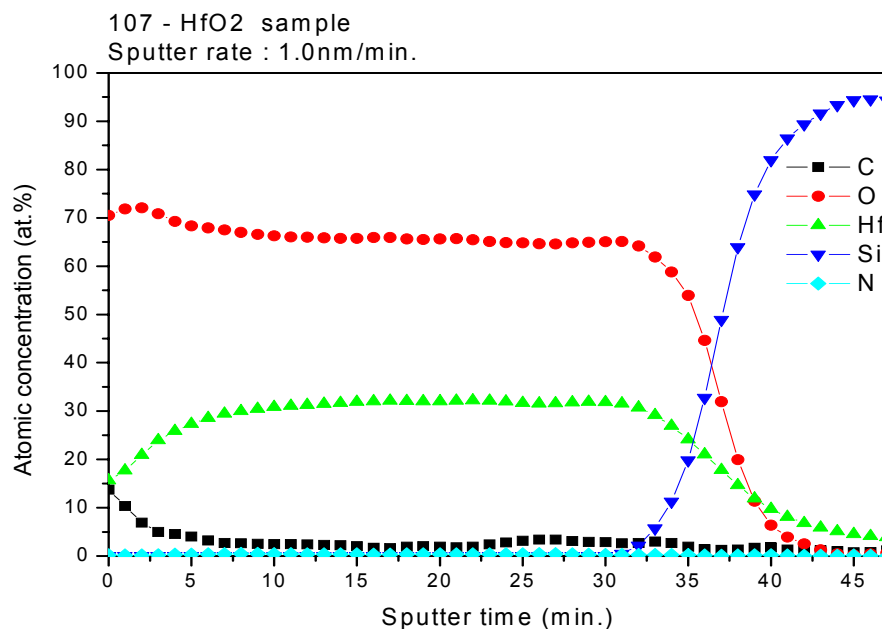


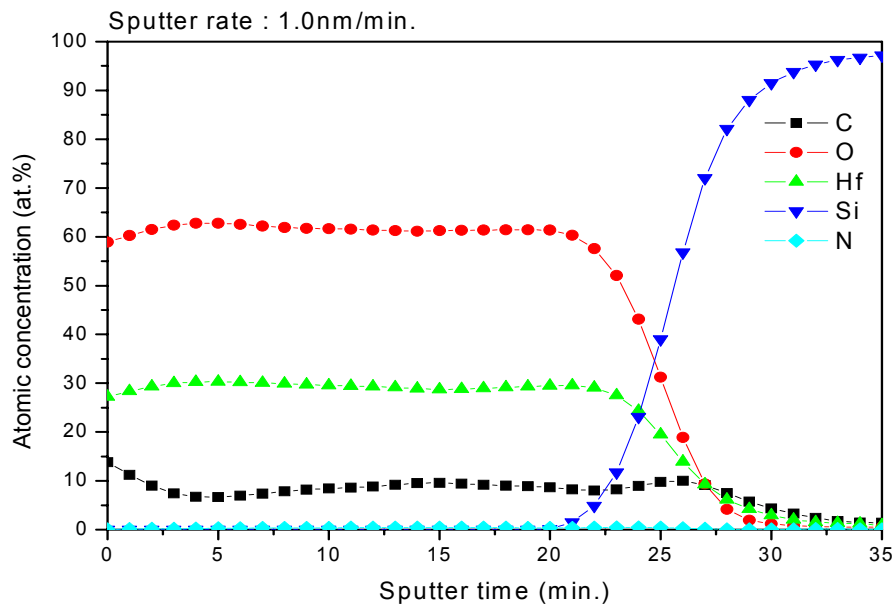
Figure 5 Stage temperature versus (a) [Hf]/[O] ratio and (b) hydrogen impurities.

In order to measure the carbon content more accurately Auger Electron Spectroscopy (AES) was used. This technique reported the C content in plasma HfO₂ films was < 2% compared to 8% in thermal HfO₂ films (figure 6).

TiN films deposited on silicon wafers showed a resistivity < 170 μΩ cm at 350°C deposition temperature. For thermally deposited TiN using NH₃ around 500°C is required to achieve similar resistivity values. It is known that impurities within thin films can cause scattering of electrons and hence a higher resistivity. This can be seen in figure 7 where an increased plasma exposure time allows for more effective chlorine removal by the hydrogen plasma (as HCl) and this is reflected by a corresponding drop in resistivity.



(a)



(b)

Figure 6 (a) AES depth profiling of TEMAH and O₂ plasma (5 second exposure time) shows around 2% carbon. (b) TEMAH and H₂O thermal shows around 8% carbon. *Analysis courtesy of Hanyang University*

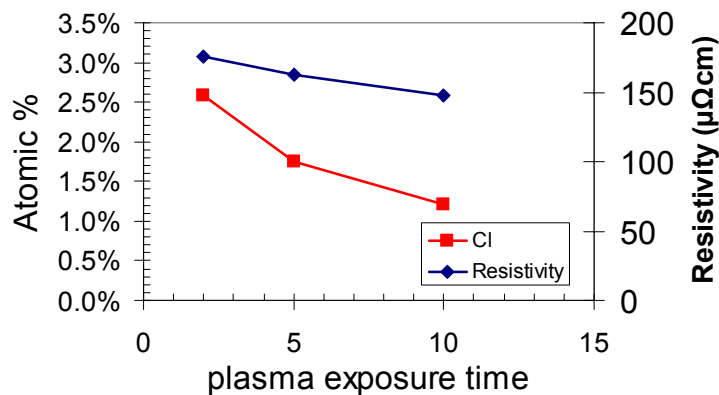


Figure 7 N₂ / H₂ plasma exposure time variation for TiN. Chlorine impurities measured by AES.

The stoichiometry of the films can be changed from being slightly nitrogen rich to titanium rich by varying the N:H gas ratios in the plasma. It is supposed that limiting the amount of nitrogen available for the reaction produces the titanium rich film. Figure 8 shows this variation with respect to refractive index. Oxygen content in the films was measured by AES to be less than 3% except for H₂/N₂ ratios greater than 40, where high oxygen (13%) was measured. This can be attributed to post deposition oxidation before sample measurement.

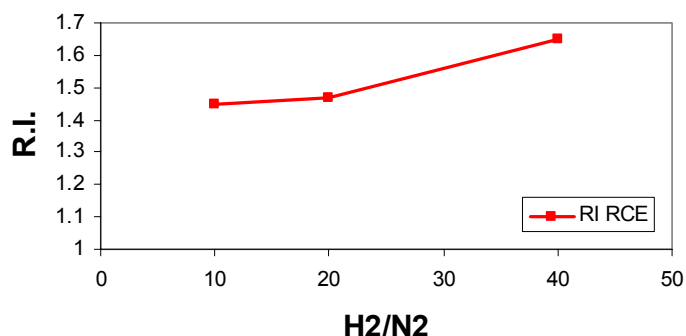


Figure 8 Refractive index measured by spectroscopic ellipsometry according to various H₂ to N₂ ratios in the plasma gas mixture.

Conclusions

The deposition of HfO₂ and TiN by thermal and remote plasma ALD was demonstrated in the Oxford Instruments FlexALTM reactor. It was shown that plasma enhanced ALD of HfO₂ resulted in a higher growth rate per cycle for O₂ plasma (1.1Å) than for H₂O (0.8Å). The plasma films showed around 2% carbon at 5 seconds of O₂ plasma exposure as opposed to 8% carbon for the thermally grown films. Low resistivity values (170μΩcm) were obtained for TiN at 350°C using plasma ALD. The influence of the N₂ to H₂ ratio in the plasma gases was investigated and found to change the stoichiometry of the film when the reaction was starved of nitrogen. For a Ti:N ratio of 1:1 it was found that the N₂:H₂ ratio should be 1:20.

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