Enhanced Dielectric Performance of HfO_2 Thin Films Via Novel Atomic Layer Deposition Conversion at Production Speed and Efficiency

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Abstract

High quality dielectric ALD films of HfO_2 and $AlHfO_x$ have been deposited at production worthy speed and efficiency. The CRISP HfO_2 process is up to three times faster than other ALD tools and uses up to 29 times less Hf-metal precursor. The dielectric properties of the films are influenced by the type of conversion, pure O_3 or the novel CRISP conversion, and the amount of Al_2O_3 introduced into the bulk HfO_2 film in a nanolaminate scheme. For HfO_2 films deposited at 250°C, Addition of Al_2O_3 at varying amount gave the highest κ, up to 18.9, improved dielectric strength up to 7.8 MV/cm, and reduced leakage current at 60V down to $8.1e^{-12}$ J. These results are a critical step to providing improved dielectric ALD films to the compound semiconductor community for dielectric barriers and MIM capacitors.

Introduction

Hafnium dioxide, HfO_2, is a high-κ dielectric barrier with exceptional stability that has been used in a litany of applications, such as the high-κ metal gate dielectric for transistors.[1] While the dielectric constant is high, ~20-25, the application of HfO_2 can be limited due to high leakage currents or low breakdown voltages. Fortunately, the addition of a secondary dielectric material, such as Al_2O_3 or Ta_2O_5, can improve the deficiencies and open new applications such as MIM capacitors. One technique to provide controlled doping or layering of a secondary oxide is atomic layer deposition, ALD.

ALD is an enabling technology for dielectric barriers over a range of device applications, from gate dielectrics to insulating barriers for a range of compound semiconductor devices such as GaN HEMT and MEMS devices.[2] Through self-limiting surface chemistry, ALD provides a conformal and pin-hole film of high quality for bulk materials at thin total thickness, <10nm over any device architecture accessible to the process gas. Due to the digital growth nature of ALD, it also has the advantage of creating nanolaminate films with vertically discrete layers of a secondary dielectric to tune the bulk dielectric properties of the full ALD film. This dielectric tuning has been exploited for multiple oxide systems, HfO_2/Al_2O_3,[3] Ta_2O_5/ZrO_2 or Al_2O_3,[4] and others,[5] with success. HfO_2/Al_2O_3 nanolaminate ALD films have found significant success at MIM-cap devices, both in conventional CMOS Si flow[6] and compound semiconductor applications, such as GaAs HBT devices.[7]

Two major drawbacks to wider adoption of ALD solutions for MIM-cap applications is the lack of speed and efficiency of the ALD processes. The root cause of this issue is that traditional ALD reactors are stuck in a process chamber pressure-based tradeoff. At high pressure, precursors are used more efficiently, but purge times suffer and at low pressures, purge times improves, but precursor efficiency degrades. Fortunately, Forge Nano has single wafer ALD technology that increases deposition rate and improves precursor efficiency. Enabled by the proprietary reactor design and fast pneumatic dosing valves, the ALD^X tool set enables faster R&D development and higher wafer throughput by breaking the purge-precursor efficiency tradeoff.[8] With deposition rates up to 12 nm/minute and precursor efficiencies up to 85%, application of high-quality ALD dielectric barriers for compound semiconductors devices is more available to the market.

Results and Discussion

To improve the properties of ALD HfO_2 films, a comparison of a standard ALD conversion step, using O_3 alone, with a novel conversion step, referred to as a CRISP conversion, was performed on the ALD^X production tool, Apollo. The CRISP conversion entrains a small amount of non-metal catalyst into the conversion precursor flow and provides a new reaction pathway for ALD surface chemistry to proceed. The ability to control the addition of small amounts of catalyst in the conversion step, not quench the O_3, is a unique feature of the ALD^X toolset.

As shown in Table I, for ALD processes at 250°C, the CRISP process increased GPC by 29%, reduced Hf-metal precursor consumption by over three times, over the O_3 only conversion. CRISP directly improves the wafer throughput and precursor consumption. The 18-minute deposition time for 20 nm of HfO_2 is the fastest the authors have observed in literature. Critically, the film properties also improved, as shown by a density increase of 7%, more ideal O:Hf stoichiometry, and a decrease of 44% in C impurities. Both

films are crystalline as deposited at 250°C and a simple Scherrer analysis shows that the CRISP process has larger crystal grains and a higher proportion of crystalline to amorphous film. Taken together, these data suggest that the overall quality of the HfO_2 film is superior to a conversion with O_3 alone.

TABLE I
HfO_2 FILM PROPERTIES FOR O_3 AND CRISP CONVERSION ON THE ALD^X TOOLSET DEPOSITED AT 250°C

	O_3 Only	CRISP	Difference
GPC (Å/cy)	0.77	0.99	29% faster
20 nm Film Deposition (hours)	0.98	0.3	3.3x faster
Hf Consumption/ 20 nm (Torr·s)	56	16	3.4x less
Density (g/cm^3)	8.3	8.9	7% more dense
O:Hf Ratio (XPS)	2.4	2.2	0.2 more ideal
C content (%)	3.2	1.8	1.4% less

Since the HfO_2 CRISP process takes advantage of surface catalysis, which provides access to different surface reaction mechanisms, the operating temperature for ALD is wider, as shown in Fig. 1 below. A stable ALD process is accessible for the HfO_2 CRISP process from 100 to 300°C, providing compatibility with a range of materials and device thermal budgets. The increase in GPC, coupled with the decrease in RI at 633 nm as the deposition temperature decreases, suggests that a combination of lower film density and higher impurity incorporation occurs in film with lower temperatures.

Using a proprietary reactor design and ALD dose valves, the ALD^X toolset allows for extremely fast cycle time and drastic reduction in precursor consumption. For HfO_2 CRISP, these tools have higher deposition rate than both batch ALD and PEALD tools by 70[9] to 300%[10] respectively. This faster deposition rate correlates to a higher wafer throughput of about 2-3 times. Notably, this unique HfO_2 process on the ALD^X toolset reduces Hf precursor consumption by 6[9]-29[10] times, when compared to published data for batch and PEALD tools. Precursor consumption is often the highest input for ALD tool OpEx, so the HfO_2 CRISP process provides a significant reduction in OpEx.

With this promising HfO_2 ALD film as a foundation, introduction of a small amount of Al_2O_3 periodically into the growing film was explored. Tuning the amount of the Al_2O_3 secondary oxide in the HfO_2 bulk has been shown in previous internal data to enhancement dielectric strength and reduce leakage current density, without sacrificing κ for bulk HfO_2 film. Full dielectric measurements were undertaken and compared with the standard O_3 conversion. A simple MIM setup was constructed of 100 nm of Au film on 4” Si wafers, 200nm dielectric (HfO_2 or $AlHfO_x$) and 100 nm of Au deposited as 2- or 3-mm electrodes patterned with a shadow mask by magnetron sputtering. Both Au films had a thin (~10 nm) layer of Ti as an adhesion layer prior to sputtering. Electrode size and regularity were checked on all samples by optical microscopy. Measurements were performed at room temperature on a Trek 601C for dielectric breakdown, an Agilent E4908A Precision LCR Meter for κ, and a Keithley 6517A electrometer for leakage current at 60V.

The results for these MIM-based measurements of the bulks HfO_2 ALD films can be found in Table II below. Interestingly, the higher density and lower impurity content observed in the CRISP HfO_2 does not translate to higher κ or dielectric strength, but does improve leakage current, for the bulk film over the O_3 process. This is unexpected as normally density and composition correlates directly with dielectric characteristics. The authors suspect that the high thickness, 200 nm, of the film deposited provided more grain boundaries to form, artificially degrading the performance of the CRISP film.

Fabrication of nanolaminate films, the addition of 1-10% of Al_2O_3 layered periodically into the growing HfO_2 film, improved the dielectric properties, depending on the thickness of the Al_2O_3 layer. Specifically, the addition of just 1% Al_2O_3 increased κ to 19.2 for the CRISP process, giving the highest value for the Al_2O_3 series with both CRISP and O_3 conversions. This data further supports a κ measurement artifact for both bulk HfO_2 films, as the κ of the bulk HfO_2 O_3 and CRISP films are artificially low, 17.6 and 16.9, and the addition of Al_2O_3, which has a κ around 8 at these deposition temperatures, increase the κ. It is more common that the addition of lower κ Al_2O_3 should decrease κ from the bulk HfO_2 value or leave it unchanged, in the absence of other factors. The authors speculate that the small amount of Al_2O_3 disrupts the crystallinity of the growing HfO_2 film, allowing for the improvement in κ, dielectric strength, and leakage current density.

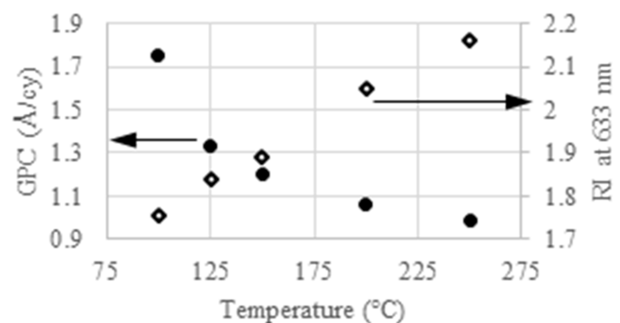

Fig. 1. GPC (solid circles, left axis) and RI (empty diamonds, right axis) for the HfO_2 CRISP process from 100 to 250°C.

All the HfO_2 films had impressive dielectric strength (dielectric field breakdown), with the highest being the 5%

Al_2O_3 in the HfO_2 O_3 film at 7.8 MV/cm. Dielectric strength appeared to be less correlated with Al_2O_3 content and more correlated with conversion process. Increasing the Al_2O_3 content in the CRISP series had no correlation with dielectric strength and both O_3 conversion samples were higher than CRISP conversion samples, regardless of Al_2O_3 content.

TABLE II
HfO_2 film Dielectric properties for O_3 and CRISP conversion on the ALD^x toolset

Film	**κ (At 10^6 Hz)**	**Dielectric Strength (MV/cm)**	**Leakage Current Density at 60V (J – A/cm²)**
HfO_2 – O_3	17.6	7.7	$3.3e^{-9}$
HfO_2 – CRISP	16.2	6.9	$2.3e^{-10}$
1% Al_2O_3 99% HfO_2 – CRISP	**19.2**	7.5	$3.3e^{-11}$
5% Al_2O_3 95% HfO_2 – CRISP	16.9	7.0	$1.1e^{-11}$
5% Al_2O_3 95% HfO_2 – O_3	17.0	**7.8**	$3.9e^{-11}$
10% Al_2O_3 90% HfO_2 – CRISP	18.9	7.4	**$8.1e^{-12}$**

Showing the flexibility of the nanolaminate ALD technique, one can minimize leakage current density by adding 10% Al_2O_3 to the HfO_2 CRISP film. This improves the leakage by 1.5 orders of magnitude, to $8.1e^{-12}$ J at 60V, from the bulk film, $2.3e^{-10}$ J, while only minimally impacting the κ, 18.9, or dielectric strength, 7.4 MV/cm. Addition of even 1% of Al_2O_3 into the bulk HfO_2 CRISP film improved leakage current by almost an order of magnitude, from $2.3e^{-10}$ to $3.3e^{-11}$ J. A similar effect is observed when 5% Al2O3 is added to the HfO_2 O_3 film. When a comparison is made between a 5% Al_2O_3 incorporation level of the O_3 and CRISP conversion, both films appear well suited for MIM cap applications. Both have a high dielectric constant, ~17, the O_3 conversion has a slightly higher dielectric constant and dielectric strength, but the CRISP conversion has a lower leakage current density.

Further tests can be undertaken to explore how often Al_2O_3 film is incorporated into the growing HfO_2 film by vertically adjusting the incorporation. In these tests, a static amount of HfO_2 film was deposited at each Al_2O_3 incorporation amount, enforcing a thicker Al_2O_3 layer at the same periodicity. Alternatively, one can keep the Al_2O_3 film thickness static and incorporate it more frequently into the growing HfO_2 film to increase incorporation content. It is expected that the method of incorporation will also impact dielectric properties of the film, providing further control over the dielectric properties. Finally, we expect increasing the deposition temperature of the films to improve dielectric properties across the board. As such, increasing the temperature of deposition up to 300°C or adding a post deposition anneal will also be explored in future work.

CONCLUSIONS

Overall, our novel HfO_2 ALD O_3-based processes have higher throughput and lower precursor consumption than comparable ALD techniques, batch ALD or PEALD. The film properties can be tuned with the addition of a CRISP component to increase deposition speed and film density, while reducing impurity incorporation and Hf precursor consumption, while opening a wider temperature range for sensitive applications. At 250°C the films high quality dielectric films are deposited and using the ability of ALD to form nanolaminate structures, the dielectric properties of the HfO_2 film can improved and tuned. With varying amounts of Al_2O_3, κ can be increased from 16.2 to 19.2, the dielectric strength can be increased from 6.9 to 7.8 MV/cm, and the leakage current density can be reduced from $3.3e^{-9}$ to $8.1e^{-12}$ J at 60V. In the future, full characterization in GaN HEMT devices is planned for both the HfO_2 – O_3 and HfO_2 – CRISP processes.

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ACRONYMS

HfO_2: Hafnium Dioxide
κ: Dielectric constant
Al_2O_3: Aluminum Dioxide
Ta_2O_5: Tantalum Pentoxide
ZrO_2: Zirconium Oxide
ALD: Atomic Layer Deposition
MIM-cap: Metal-Insulator-Metal Capacitor
GaN: Gallium Nitride
HEMT: High-Electron-Mobility Transistor
HBT: Heterojunction bipolar device
MEMS: Microelectromechanical Systems
CMOS: Complementary metal-oxide semiconductor
GaAs: Gallium Arsenide
CRISP: Catalyzing Reactions for Induced Surface Process
OpEx: Operation Expense
O_3: Ozone
PEALD: Plasma Enhanced Atomic Layer Deposition
GPC: Growth per Cycle
RI: Refractive Index
LCR: Inductance (L), Capacitance (C), and Resistance (R) meter