RESEARCH ARTICLE

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Comparison between Single Al_2O_3 or HfO_2 Single Dielectric Layers and their Nanolaminated Systems

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Plasma Enhanced Atomic Layer Deposition (PEALD) technique has been used for the fabrication of nanolaminated Al_2O_3-HfO_2 thin films as well as of single Al_2O_3 and HfO_2 layers on silicon substrates. The three different layers, i.e. Al_2O_3, HO_2 and the nanolaminated Al_2O_3-HfO_2 thin films, which consists of very thin alternating layers of Al_2O_3 and HfO_2, have been deposited at temperature as low as 250°C. Each of them possesses a total thickness of about 30 nm and has been tested as possible dielectric for microelectronics devices. In particular, the structural properties and their evolution upon annealing treatment at 800°C have been investigated. Moreover, the dielectrical properties of the nanolaminated system have been compared to the opposite single Al_2O_3 and HfO_2 layers. The collected data pointed out to promising properties of the fabricated nanolaminated film.

Introduction

Nanolaminates are composite films consisting of alternating layers of different materials [**1**]. These multilayered nanostructures have attracted great attention for the possibility of tuning their mechanical or physical properties for several and differently specific applications. In microelectronics, for instance, their possible implementation has been considered in relation to their properties as dielectric insulators [**2,3**]. In fact, huge efforts are nowadays devoted to the fabrication of multicomponent systems having high dielectric constants and good chemical/thermal stabilities. In particular, the Al_2O_3-HfO_2 nanolaminated films seem to be the most promising system to be used for silicon based microelectronics devices [**4-9**] as well as in next generation power electronics devices [**10-15**]. The possibility to have advantage from the most suited properties of each single Al_2O_3 and HfO_2 materials motivated the study of their combination as laminated systems. In fact, it is well-known that the Al_2O_3 possesses great excellent chemical and thermal stability, large band gap (around 9 eV), large band off-set with different semiconductors substrates, but by contrast, its growth provides the formation of a high oxide trap charge density and it does not a high dielectric constant value (about 9) [**16**]. Moving to the HfO_2 dielectric oxide, a quite high dielectric constant value (about 25) could be achieved, but low reliability because of its structural transition from amorphous to monoclinic crystalline at relatively low temperature (about 500°C) and high leakage current density because of its quite small band-gap (5.5eV) [**16**].

In this context, nanolaminated structure composed of the two Al_2O_3-HfO_2 high-k oxides is a promising solution for enhancing thermal stability and sustain a high dielectric constant value.

On the other hand, the fabrication of multilayered systems requires deposition techniques possessing good thickness control at nanometric scale. In this perspective, among the several growth methods, the ALD technique provides the conformal and uniform film deposition on large area, with precise thickness control at relatively low deposition temperatures [**17,18**]. In fact, ALD process is going through a rapid affirmation due to the peculiarities of its deposition mechanism. In particular, ALD is based on a sequence of self-limiting semireactions so that it is characterized of the layer-by-layer growth mode. The ALD technique originates as a thermally-driven process. Therefore, it is conventionally known as Thermal-ALD. However, more recently, an innovative kind of ALD referred as Plasma Enhanced-ALD (PE-ALD), has been widely implemented for many growth processes. The PE-ALD has been defined as an energy-enhanced deposition technique because it is based on the plasma employment to enhance the co-reactans reactivity by a plasma ignition. The principle advantage of the PE-ALD processes is a faster rate with respect the analogous thermal process.

In this study, we fabricated on Si (100) at a low temperature of 250°C by plasma enhanced atomic layer deposition, three dielectric thin films, namely Al_2O_3, HfO_2 and their combination as Al_2O_3-HfO_2 nanolaminated system. The physical properties of the Al_2O_3-HfO_2 nanolaminated films have been compared to the opposite Al_2O_3 and HfO_2 single layers. In particular, the structural characterization has been performed before and after an annealing process at 800°C in nitrogen atmosphere and the thermal stability has been evaluated. Moreover, a comparison of the electrical characteristics has been carried out to evaluate the impact of the Al_2O_3 mixing with HfO_2. It will be shown that the nanolaminated system results promising with respect to the parents Al_2O_3 and HfO_2 films.

Experimental

Materials

Al_2O_3 and HfO_2 films were deposited using trimethylaluminum (TMA) as aluminum precursor and tetrakis-dimethylamino hafnium (TDMAHf), respectively. Both metal precursors were purchased by Air Liquid as bubblers. The TMA is a liquid precursor and it was used at room temperature, while the hafnium precursor, which is a solid at room temperature, was heated at 75°C [**19**]. Both were delivered from the bubbler to the reactor chamber with N_2 carrier gas at a flow rate of 40 sccm. Depositions were carried out on (001) Si substrates.

Film deposition parameters

Films were deposited on PE ALD LL SENTECH Instruments GmbH reactor. The ALD system is equipped with a remote capacitively coupled plasma (CCP) source. It is excited by a 13.56 MHz RF generator via a matchbox. The power supply was 200 W and the oxygen-gas-flow-rate was 150 sccm.

Depositions were carried out at 250°C and at a reactor chamber pressure of 20 Pa.

For the Al_2O_3 deposition, the pulse times of metal precursor and oxygen pulse were 0.06s and 1s, respectively. For the HfO_2 deposition, the pulse times of metal precursor and oxygen pulse were 0.06s and 5s, respectively. After each precursor pulse, the deposition chamber was purged with 40 sccm N_2 for 2s, to remove un-reacted precursors. The Al_2O_3-HfO_2 nanolaminated films were deposited by repeating a unit cycle for precise thickness control. In particular, the Al_2O_3-HfO_2 nanolaminated film consisted of twenty total layers. Each Al_2O_3 or HfO_2 layer has been obtained by five unit cycles, with a unit cycle comprising a precursor, purge, oxygen reactant, and final purge.

All the deposited films were annealed by rapid thermal annealing process, which was carried out at 800°C in N_2 atmosphere for 1 minute in a Jetfirst 150 JIPELEC furnace.

Structural and morphological characterizations

Microstructures were investigated by transmission electron microscopy (TEM) using a FEG-TEM JEOL 2010F. Morphological characterization was performed by atomic force microscopy (AFM), which was carried out on a Digital Instrument D3100 operating in air.

Device fabrications

The test-patterns for the electrical characterization were fabricated using top Ni/Au electrodes. On the deposited films, Ni/Au bilayers, consisting of 80 nm of each metal, were deposited by sputtering and patterned by standard optical lithography and lift-off technique, to fabricate circular diodes.

The dielectric constants were determined by capacitance voltage (C–V) measurements, which were carried out using a Karl-Suss probe station equipped with a Agilent B1500A parameter analyzer.

Results and discussion

Single Al_2O_3 and HfO_2 layers, with the same thickness, have been deposited by plasma enhanced atomic layer deposition (PE-ALD).

Common deposition parameters which have been used for the growth of the two different films consisted in deposition temperature of 250°C, 200 W plasma power, a nitrogen gas carrier for the two metal precursors and a deposition pressure of 20 Pascal, while the other parameters which needed to be different for the growth of the two Al_2O_3 and HfO_2 layers and have been summarized in **Table 1**.

Table 1. Specific deposition parameters for the growth of Al_2O_3 and HfO_2 thin films.

Film	Number of cycles	Metal Precursor/purge	O_2 Plasma/purge
Al_2O_3	250	0.06s/2s	1s/2s
HfO_2	200	0.01/5s	0.3s/2s

The growth rates of the Al_2O_3 and HfO_2 processes have been evaluated to be 1.1 Å/cycle and 1.6 Å/cycle, respectively.

The superficial morphology has been investigated by AFM characterization. In **Fig. 1** are shown the AFM bidimensional maps recorded on 1µm × 1µm areas for the two kinds of thin films. Their morphologies show very smooth surfaces as confirmed by the calculated root mean square (RMS) values, namely 0.08 nm and 0.09 nm, for Al_2O_3 and HfO_2 thin films, respectively. These values are also comparable with the RMS of the bare silicon substrate (0.05 nm), and indicated that a layer-by-layer ALD growth occurred.

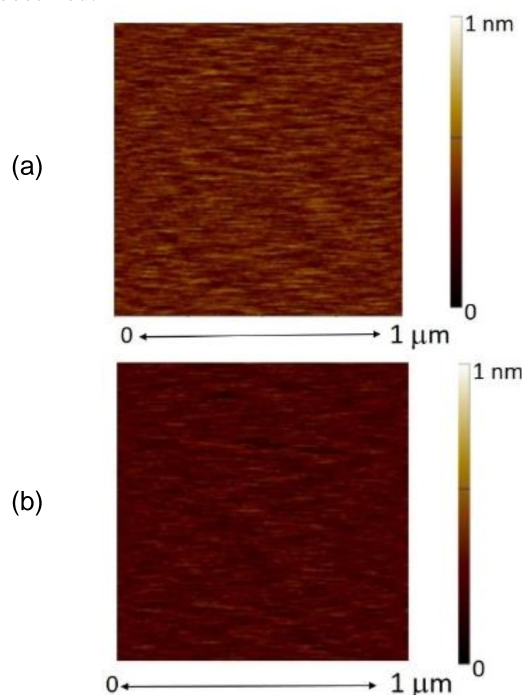

Fig. 1. AFM bidimensional maps of Al_2O_3 (a) and HfO_2 (b) thin films grown by PEALD on (001) Si substrates.

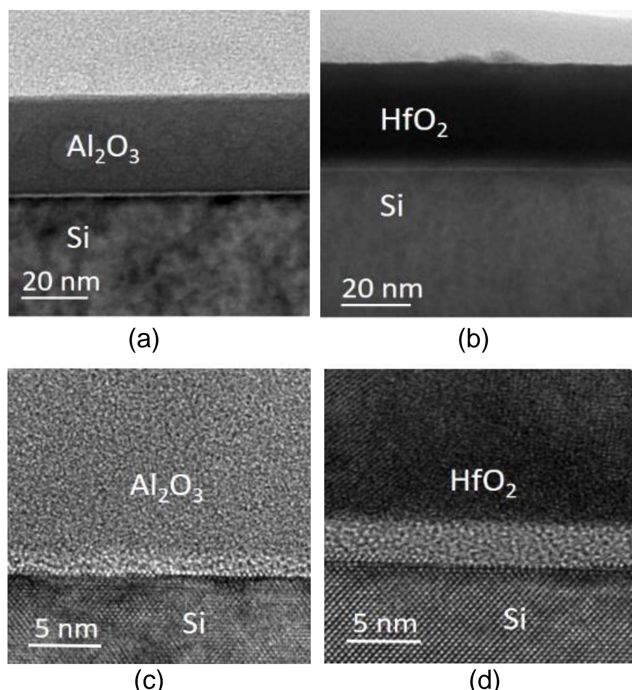

Fig. 2. TEM cross-images to compare structural properties between PEALD Al_2O_3 (a) and HfO_2 (b) as-deposited films. The same comparison has been carried out after the annealing at 800°C in N_2 atmosphere of both films, namely Al_2O_3 (c) and HfO_2 (d).

Al_2O_3 as-deposited film possesses a uniform thickness of about 30 nm and is amorphous as well as adherent to Si substrate, as demonstrated by cross-section TEM image in **Fig. 2a**. However, despite the initial amorphous nature, a crystallization process of the Al_2O_3 occurred under electron beam irradiation, during TEM analysis. The crystallization phenomenon begins at the film/substrate interface and generates a polycrystalline structure. Actually, this is an already known phenomenon reported literature [**20**], and it is related to the interaction with energetic particles, causing elastic interactions and/or excitation-related processes, which provides energy for the breaking or rearrangement of unstable bonds [**21**]. This mechanism depends on both the incident electron-energy and exposure times. Moreover, the electron irradiation can determine two types of damage processes, namely the elastic displacement and the excitation-related processes, which are dominant at higher or lower electron energy ranges, respectively [**20**]. Al_2O_3 thin films fabricated by several deposition techniques showed some transition from amorphous to polycrystalline α-alumina phase after irradiation by 300 and/or 200 kV electron beam has been also reported [**22,23**].

Similarly to the Al_2O_3 layers, HfO_2 thin films have been also deposited by PEALD and investigated by TEM analysis. In **Fig. 2b,** the HfO_2 30 nm film appears amorphous and no modification occurred under electron beam investigation. Probably because of the higher film density with respect to Al_2O_3 ($d_{HfO2} = 9.68$ gr/cm^3 and $d_{Al2O3} = 3.95$ gr/cm^3) and atomic weight of the Hf^{+4} cations. However, since it is well-known that the crystallization temperature of the HfO_2 films is about 500°C [**24**] and that the observed Al_2O_3 crystallization could be indication for low thermal stability of the deposited films, an annealing treatment has been performed at 800°C in N_2, in order to simulate some device steps processing. TEM images in **Figs. 2c and 2d** demonstrated that the annealing treatment did not produce any alteration of the structural properties of Al_2O_3 film, while a crystallization of the HfO_2 film is quite evident.

Finally, the dielectric behavior has been investigated by the capacitance-voltage (C/V) measurements which have been showed in **Fig. 3**. Dielectric properties of the two samples have been evaluated by fabrication of test-patterns which has been performed in several steps. The C/V curves have been measured at 1 MHz and the accumulation capacitances have been used to determine the dielectric constants. The dielectric constant value of the Al_2O_3 is 7.8, while in the case of HfO_2 films have been evaluated to be about 13.

The comparison between the two deposited films suggests a better dielectric thermal stability of the Al_2O_3 film with respect to that of HfO_2 layer, while this last possess a higher dielectric constant value. The results are in agreement with the predicted behavior from the literature data [**10,24**] and their combination as laminated system has been considered in order to get the improved performances.

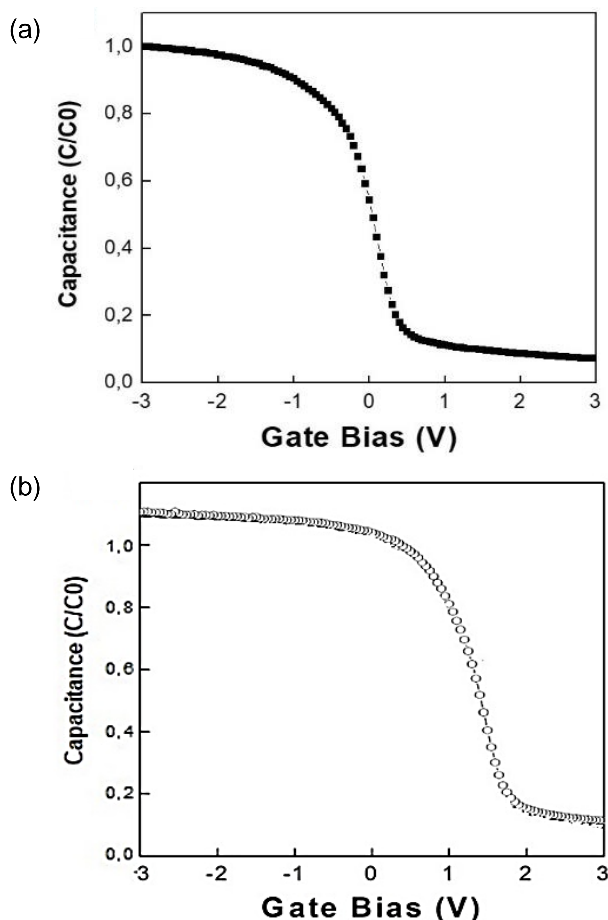

Fig. 3. C-V curves of Al_2O_3 (a) and HfO_2 (b) films deposited by PE-ALD method recorded at 1 MHz.

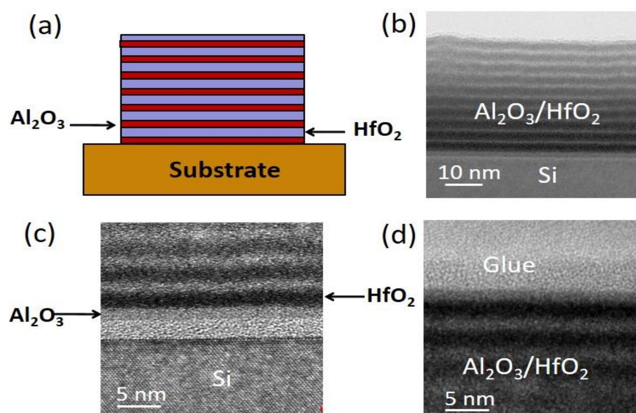

Fig. 4. Schematic of the Al_2O_3/HfO_2 laminated film (a) and its cross section TEM image (b). The TEM magnification (c) shows the formation of about 1.6 nm alternating Al_2O_3 and HfO_2 thin layers in the as-dep film, whose interfaces became not so defined after annealing, as shown in the TEM image (d).

The proposed laminated system is schematically shown in **Fig. 4a** and it consists of a 10 stacked Al_2O_3/HfO_2 bilayers, with each sub-layer thickness minor than 2 nm. This nanolaminated film has been fabricated by the same main deposition parameters used for the growth of the single layers, i.e. deposition temperature, process pressure and plasma value, while the cycles sequence has been appropriately modified. In particular, different precursors have been alternatively pulsed into the reactor chamber and extended purge time has been carried out to clean residual precursors on both growing substrate and the entire chamber to avoid cross contamination between different precursors.

The formation of the desired nanolaminated film has been corroborated by TEM investigation. In fact, in **Fig. 4b** the laminated film is clearly visible, it possesses 36 nm thickness, many interfaces have been formed and each Al_2O_3 or HfO_2 layer possesses a 1.4-1.8 nm thickness. In the TEM magnification, the HfO_2 sub-layer shows a thickness slightly higher than those of the Al_2O_3, however, this could be also due to the darkest mass contrast of the HfO_2 with respect to the Al_2O_3.

The thermal stability of the laminated samples has been investigated by the annealing treatment at 800°C in N_2 atmosphere which has been previously performed on the single layers. TEM image (**Fig. 4c**) showed that no evident structural evolution occurred upon annealing process. The annealing treatment resulted in a small decrease (about 2 nm) of the total thickness because of a densification process. In addition, diffusive phenomena, activated by high temperatures, favored an initial intermixing process between Al_2O_3 and HfO_2 nanolayers, in fact in TEM image after the annealing process less sharp interfaces are evident. The most important results, however, it is represented by the amorphous nature of the laminated films which has been confirmed by diffraction image not showing any diffraction spot except those from the silicon substrate (**Fig. 4d**). The missed crystallization process, upon annealing at temperature well beyond the HfO_2 crystallization value (500°C), is a very important result suggesting that the laminated dielectrics are a promising solution to improve the thermal stability of the deposited dielectrics.

In addition to the studies on the structural properties, the morphological characterization has been performed using AFM investigation. The AB bilayer sample possesses a rounded grain surface morphology with root mean square of the height distribution (RMS) values of 0.58 nm, slightly higher than the values found in the single Al_2O_3 and HfO_2 single layers, probably because of the roughness of several interfaces. However, the laminated samples showed a similar morphology and similar RMS values before and after the annealing treatment. A representative AFM bidimensional map of laminated samples is reported in **Fig. 5**.

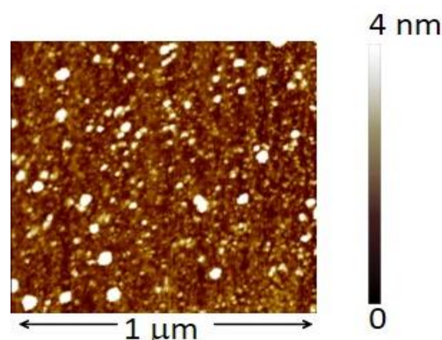

Fig. 5. AFM bidimensional map of Al_2O_3/HfO_2 nanolaminated thin film grown by PEALD on (001) Si substrates.

A complete electrical characterization has been performed by the capacitance voltage (C-V) curves reported in **Fig. 6**. They have been used to experimentally determine the dielectric constant values and other dielectric parameters, such as the flat band voltage which is related to the number of charged defects and the hysteresis which is associated with the number of trapped (negative) charges. The dielectric constant value of the laminated film is about 10. The shape and the position of the C-V characteristics are directly related to the amount of charged defects in the insulator and at the insulator/semiconductor interface.

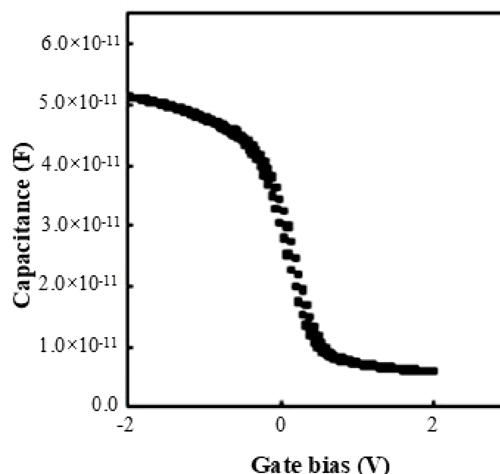

Fig. 6. C-V curves of Al_2O_3/HfO_2 nanolaminated films deposited by PE-ALD method recorded at 1 MHz.

In fact, the unbalanced charges arising from defects will cause a C-V curve shift moving the flat band voltage from the ideal condition. In the case of Ni based contacts, the ideal flat band voltage value has been calculated to be $V_{FB\ Theor}= (\Phi_{Ni}- \psi_s)/q = - 0.25V$, where Φ_{Ni}.is the nickel work function and ψ_s= is the position of the Fermi level in the p-type silicon substrate. The shift value between the theoretical ($V_{FBTheor}$) and experimental (V_{FB}) can be used to quantify the number of fixed charges (N_f [cm^{-2}]) in the dielectric film using the equation:

$$N_f = \frac{C_{ox}\Delta V_{FB}}{eA}$$

where C_{ox} is the accumulation capacitance, e is the elementary electron charge, A is the area of the gate and ΔV_{FB} is the flat band shift.

In addition, by the flat band shift between the backward and forward C-V curves (hysteresis), the oxide trapping states (N_{ot}) can be quantified.

The estimated N_f and N_{ot} values are $N_f = 2.06 \times 10^{12}$ cm^{-2} and $N_{ot} = 1\times10^{11}$ cm^{-2}, respectively.

The comparison of the complete structural and dielectric data of single Al_2O_3 or HfO_2 and their laminated combination, pointed out that the nanolaminated can be considered a promising system. In fact, it showed an amorphous structure before and after the annealing treatment and a better dielectric behavior in terms of dielectric constant and charge traps amounts.

Conclusion

Huge efforts are nowadays devoted to the fabrication of multicomponent systems having high dielectric constants and good chemical stability. In particular, Al_2O_3 and HfO_2 oxides might be combined on the basis of their intrinsic physical properties.

Three dielectric layers, namely Al_2O_3, HfO_2 and Al_2O_3/HfO_2 laminated, have been deposited on silicon substrates by PEALD with the same thickness and their thermal stability and dielectric properties have been compared. The Al_2O_3 layer possesses good thermal stability but low dielectric constant. The HfO_2 layer possesses the highest dielectric constant value (about 13) but low thermal stability and as a consequence highest leakage current density and lowest reliability, while the combination of aluminum oxide and hafnium oxide in nanolaminated system improved the relatively low thermal stability of HfO_2 (~500°C) and increased the relatively low dielectric constant (~ 8) of Al_2O_3 thin films.

Author's contributions

Conceived the plan: R. L., F. R.; Performed the expeirments: E.S., P. F.; Data analysis: R. L., E. S. P. F., F. R; Wrote the paper: R. L. Authors have no competing financial interests.

Keywords

Dielectric, nanolaminates, atomic layer deposition, plasma enhanced deposition process.

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