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Optical and dielectrical characterization of atomic layer deposited Nb2O5 thin films

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Optical and Dielectric Characterization of Atomic Layer Deposited Nb_2O_5 Thin Films

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Nb_2O_5 films were grown by atomic layer deposition using (tert-butylimido)tris(diethylamido)niobium as the niobium source and ozone as the oxygen source. The effects of deposition and post-deposition annealing conditions, physical thickness as well as the phase composition on the dielectric properties of Nb_2O_5 thin films have been investigated. In addition, the optical properties of the films have been evaluated. It was found that by tuning the deposition parameters and post deposition treatments it was possible to obtain high k-values up to 120 with reasonably low leakage current.
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The scaling down of future dynamic random access memories (DRAM) requires a dielectric material with high permittivity and low leakage current. Atomic layer deposition (ALD) has been adopted as the deposition technique in microelectronics industry due to its unique self-limited growth mode providing inherent conformality, repeatability and quality of the films.[1] As an alternative to the current ALD $ZrO_2/Al_2O_3/ZrO_2$ used nowadays in production line, $Sr_xTi_{(1-x)}O_y$ (STO) and the rutile phase of TiO_2 are considered as the most promising materials. However, the corresponding ALD processes still need improvement. For example, the formation of the high permittivity rutile phase of TiO_2 usually requires either high deposition temperature and/or post-deposition annealing. In addition, high work-function ruthenium electrode material is needed, which can become a cost issue.[2,3] Issues concerning STO are related to the difficulty to obtain composition uniformity as well as to the possibility of crack formation upon crystallization leading to high leakage current.[4]

Nb_2O_5 is a wide bandgap (3.6 eV) dielectric material with a high index of refraction (n = 2.4) and permittivity (29 to 200 depending of the crystalline phase[5]). The electrical properties and potential DRAM application of Ta_2O_5/Nb_2O_5 bi-layer grown by ALD using $Nb(OEt)_5$[6,7] or NbF_5[8] as the niobium precursor have been reported. Dielectric behavior of Nb_2O_5 grown by ALD from the NbI_5/O_2[9] precursor combination has also been reported. The Nb_2O_5 films were found to be very leaky. Annealing in oxygen greatly reduced the leakage current but also considerably increased the capacitance equivalent thickness (CET) which was probably due to the growth of low permittivity SiO_2 interfacial layer during annealing.

This letter reports unprecedented high k-values for Nb_2O_5 thin films grown by ALD on TiN, using the recently reported novel ALD process.[10] Ozone (Wedeco Ozomatic modular 4 HC Lab Ozone, ozone concentration 100 g/m^3) and (tert-butylimido)tris(diethylamido)niobium (TBTDEN) (ATMI, USA) were used as the oxygen and niobium sources.

Nb_2O_5 thin films were grown on TiN covered Si substrates in a hot-wall flow type F-120 ALD reactor (ASM Microchemistry Ltd.). The films were deposited in the temperature range of 150–325°C. The pulsing sequence of 0.7/1.0/1.0/1.5 s for niobium source/purge/oxygen source/purge was used. Nitrogen (99.999%) was used as a carrier and purge gas. Some of the films were annealed after the deposition at different temperatures for 20 minutes in a tube furnace under nitrogen. Electrical characterization of the films was carried out on $Al/Nb_2O_5/TiN/p\text{-}Si(100)/Al$ capacitors. The top electrodes consisted of 100–110 nm thick Al dots with an area of 0.205 mm^2 E-beam evaporated through a shadow mask. The current–voltage (I–V) curves were measured with a Keithley 2400 Source Meter in the stair sweep voltage mode. The voltage step was 0.05 V and the top electrodes were biased negatively in relation to the TiN/Si substrate, i.e. electrons were injected from the top electrode. Capacitance values were measured at zero bias voltages in C-V measurements performed with an HP4284A precision LCR-meter in a two-element series circuit mode. The frequency of the AC signal was 1 kHz. The k-values of the films were calculated from the mean capacitance values measured from 10 dots at various areas of the sample. The refractive indexes of the films were measured with a M-2000D (1.25–6.5 eV) spectroscopic ellipsometer from J.A. Woollam. Measurements were performed on a goniometric stage at an incident angle of 75°.

The deposition temperature had a critical influence on the refractive index of Nb_2O_5 thin films in the as-deposited state. The refractive index at 550 nm varied from 2.05 to 2.39 when varying the deposition temperature from 125 and 325°C (Figure 1). The refractive index of the films deposited in the temperature range of 150–200°C increased upon post-deposition annealing at 600°C. Annealing did not have a particular effect on the refractive index of the films deposited at higher temperatures. This is consistent with the previously published data[10] which revealed a high carbon content in the films deposited at low temperatures, reported to be the reason for the low refractive index.[11] The increase of the refractive index may also be related to an increase in density.[12,13] When the deposition temperature is increased, the mobility of the surface species increases leading to denser films. XRR showed an increase of the density from 3.9 to 4.5 g/cm^3 when increasing the deposition temperature from 150 to 250°C. Further increase of the deposition temperature from 250 to 300°C did not show any further influence on the film density. After annealing, the differences in refractive index between the films grown at different temperatures were greatly reduced (Figure 1). Post-deposition annealing treatment is known to induce densification of the

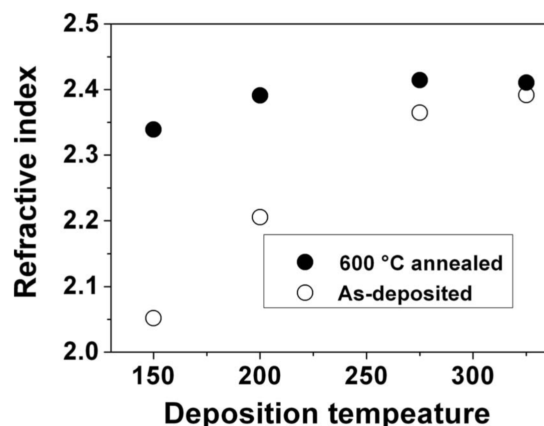

Figure 1 Refractive index at 550 nm for 30 nm thick Nb_2O_5 films as a function of the deposition temperature.

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Table 1. K-values of 30 nm thick Nb_2O_5 films deposited and annealed at various temperatures.

	Deposited at 250°C			Deposited at 275°C			Deposited at 300°C		
Annealing temperature (°C)	As-dep.	550	650	As-dep.	550	650	As-dep.	550	650
k	55	42	61	47	105	58	55	71	67

films and has also been shown to decrease the amount of impurities in the films.[14]

In order to study the influence of the deposition temperature on the dielectric properties a series of 30 nm thick Nb_2O_5 thin films was deposited at 250, 275 and 300°C. The corresponding k-values are summarized in Table I. In the as-deposited state, the films presented similar k-values (Table 1). The effect of the annealing temperature and the resulting phase change from amorphous to orthorhombic Nb_2O_5 (ICSD card 1840) has also been investigated. The crystallization temperature of Nb_2O_5 thin films with thicknesses ranging from 15 to 60 nm has been previously determined to be around 550°C.[10] XRD patterns of 30 nm thick Nb_2O_5 films deposited at 250, 275 and 300°C and annealed at 550 and 650°C have been recorded (Figure 2a and 2b). When annealed at 550°C, the films deposited at 250°C remained amorphous whereas the films deposited at 275 and 300°C crystallized to the orthorhombic phase. When annealed at 650°C, all the films became crystallized. An increase in the deposition temperature led to a higher peak intensity which indicates higher state of crystallization. A higher deposition temperature favors more complete crystallization and lowers the crystallization temperature.

Crystallization upon annealing increased the k-values (Table 1). High k-values ranging from 55 to 105 were measured. The growth of low-permittivity interface layers between Nb_2O_5 and bottom electrode can lower the permittivity values when using high annealing temperature. The permittivity of the film deposited at 275°C decreased from 105 to 58 when annealed at 550 and 650°C, respectively. Therefore, formation of the orthorhombic phase of Nb_2O_5 clearly improved the permittivity values of the films but high crystallinity obtained at high annealing temperatures seems to be detrimental to the permitivitty value. Therefore deposition temperature of 275°C and annealing temperature of 600°C were chosen for further investigation.

The relation between the thickness and the permittivity of Nb_2O_5 thin films was investigated. Strong dependence between permittivity and physical thickness (Figure 3) was observed for both as-deposited and annealed films. The drop in the permittivity in thinner films could be explained by a larger effect of the interfaces as compared to the film´s bulk. This behavior exhibited by dielectric thin film, as in the case of STO,[4,15] has been described as a so called "dead layer" effect.[16,17] However, this phenomenon is still not fully understood and it is still under investigation whether extrinsic and/or intrinsic effects are provoking it.[18]

The k-values varied in the range of 18 to 77 and from 25 to 125 for the as-deposited and crystallized films, respectively, when the film thicknesses varied between 13 and 45 nm.

We observed that the crystallized films had lower leakage currents than the amorphous films. For example the as-deposited 30 nm thick Nb_2O_5 film deposited at 300°C had a leakage current density of 10^{-4} A/cm^2 at 1 V whereas when annealed the leakage current dropped two orders of magnitude to 10^{-6} A/cm^2 at 1 V. It has usually been reported that crystallized films present higher leakage due to current propagation along the grain boundaries.[19,20] The optical band gaps extracted from ellipsometry measurements present an increase of 0.3 eV for the crystallized Nb_2O_5 compared to the as-deposited films. This suggests a higher band offset between the high-k Nb_2O_5 layer and the electrodes, resulting in lower leakage currents for crystallized films.

It should be noted that with lower Nb_2O_5 film thickness, the leakage current density increases. For example, Nb_2O_5 films with thicknesses below 25 nm exhibited higher leakage, generally in the order of 10^{-5} A/cm^2 at 1 V, even after crystallization. This has been observed in many cases with various high-k oxides.[21] Possibly, a doping with Al_2O_3, as in the case of TiO_2[3,22] could decrease the leakage current and this work is ongoing.

In summary, this work presents interesting dielectric properties of Nb_2O_5 films for memory applications. The dielectric properties are sensitive to deposition and post-deposition treatments, and a careful tuning of those for targeted performances is required. Furthermore, the understanding on the influence of the deposition and annealing temperatures on the formation of the orthorhombic phase and degree of crystallization, and their possible influences on the formation of a low permittivity layer, is certainly a key issue for optimization of the dielectric properties of atomic layer deposited Nb_2O_5 thin films.

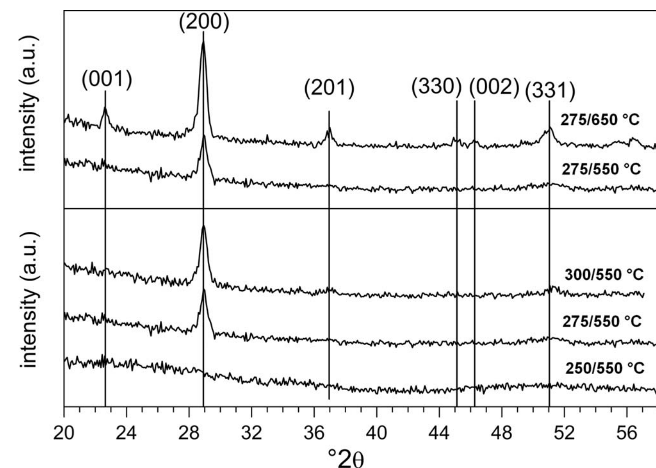

Figure 2 XRD patterns of 30 nm thick films with different deposition/annealing temperatures. Miller indexes are listed for reflections attributable to the orthorhombic phase of Nb_2O_5 (ICSD card 1840).

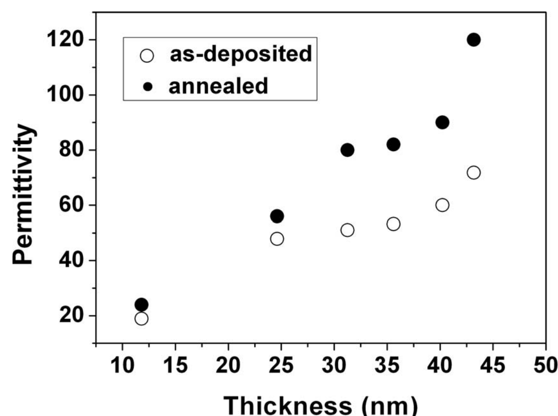

Figure 3 physical thickness effects on the k-values of Nb_2O_5 thin films as-deposited and annealed at 600°C.

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