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GROWTH AND CHARACTERIZATION OF Al_2O_3:HfO_2 NANOLAMINATE FILMS DEPOSITED BY ATOMIC LAYER DEPOSITION (ALD)

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As gate dielectrics in logic and memory continue to scale, higher dielectric constant materials, such as Al_2O_3, HfO_2, ZrO_2 and others are under investigation to replace silicon dioxide. Nanolaminates of these high-K films are easily grown by Atomic Layer Deposition (ALD) and may offer potential benefits by combining the best properties of each metal oxide into one composite film. The physical and electrical properties of Al_2O_3: HfO_2 nanolaminate films, grown by ALD, were investigated for compositional ranges from 4%-96% HfO_2 in Al_2O_3. The ALD deposition technique results in good within wafer electrical thickness uniformity (1-2%, 1 sigma). The deposition kinetics of the nanolaminates shows good nucleation on SiO_2 surfaces and deposition rates intermediary between Al_2O_3 and HfO_2. The microstructure the as-deposited films, as determined by TEM cross-section, is observed to be amorphous (depending on Hf content) with smooth interfaces to the bottom interfacial layer and top polysilicon. Compositional analysis, as determined by Medium-energy ion scattering (MEIS)and spectral ellipsometry, shows that the ratio of Al_2O_3 to HfO_2 can be tuned effectively by adjusting the pulse ratio of the two films in the nanolaminate growth process. Poly-gate capacitor results show that the nanolaminates exhibit 4-7 orders of magnitude lower leakage current than SiO_2 of the same electrical thickness, depending on the film composition. C-V measurements indicate that the flatband of these films can shift as much as 300-450 mV from thermal oxide. Hysterisis is present and charge trapping in the nanolaminates is more severe than in the individual metal oxide films.

INTRODUCTION

As the drive to shrink the gate dielectric in CMOS devices continues, many high dielectric constant materials, such as HfO2 and their silicates and derivatives are under consideration [1,2]. With the advent of Atomic Layer Deposition (ALD) [3], it has been shown by some groups that nanolaminates of these high-K films can be made [4-6]. This enables an entire new class of potential gate dielectric candidates, which may possess desirable characteristics. Here, we examine the growth kinetics, material properties and electrical characteristics of ALD nanolaminates comprised of Al_2O_3 and HfO_2 in different compositions. This system is attractive since it combines the good high temperature thermal stability of Al_2O_3 with the higher-K value (20) of HfO_2.

Nanolaminates of different compositions can be easily deposited by alternately sequencing X pulses of one metal oxide followed by Y pulses of the other. Since the deposition rate (A/pulse) of each metal oxide is known, the approximate composition,

based on film thickness can be determined. For instance, the ALD deposition rate of these films were 0.81 A/pulse for Al_2O_3 and 0.49 A/pulse for HfO_2. Alternately depositing 1 cycle of Al_2O_3 followed by 2 cycles of HfO_2 results in a nanolaminate containing 45% Al_2O_3. Nominal nanolaminate composition as a function of Al_2O_3:HfO_2 pulse ratio is shown in Figure 1.
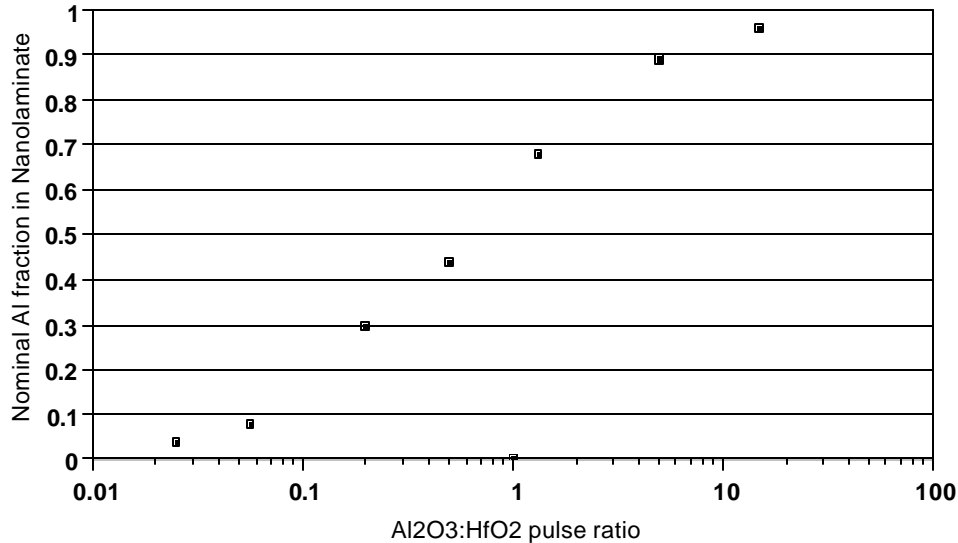

Figure 1: Al_2O_3:HfO_2 pulse ratio vs. Nominal Al_2O_3 thickness fraction in nanolaminate. Films are deposited on top of chemical oxide.

EXPERIMENTAL

ALD growth of the nanolaminates was done in a commercial ALD reactor at 300 C. Al_2O_3 cycles were deposited using tri-methyl aluminum (TMA) and water, while HfO2 cycles were deposited using $HfCl_4$ and water. P-type monitor wafers (11-25 ohm-cm) were used for the experiments. They were cleaned in an automated wet deck with megasonics and chemical oxide was grown using a modified RCA clean. Thermally grown interfacial layers were grown in a commercial single wafer cluster tool. Polysilicon gate capacitors were fabricated using a CMOS process flow, modified for high-K gate dielectric [7].

Refractive index, film composition and density were measured using a commercial spectral ellipsometer coupled with X-ray detection of film thickness. Composition was also determined by Medium energy ion scattering (MEIS). Atomic force microscopy was done on a Digital AFM in tapping mode. The average rms and Rmax of 2 scans (1 um x 1 um) across each surface was reported. Cross-sectional transmission electron microscopy (TEM) was also performed using a commercial system.

RESULTS AND DISCUSSION

Growth Kinetics of Nanolaminates :

ALD nanolaminates are deposited by successively delivering one or more cycles to the substrate of one component (e.g. Al_2O_3) followed by one or more cycles of another component (e.g. HfO_2). Since the mechanism of nanolaminate film growth is similar to that of the individual metal oxides, the growth behavior follows the same linear trends. Figure 2 shows the growth curves of Al_2O_3, HfO_2 and the 1:1 Al_2O_3:HfO_2 nanolaminate (nominal fraction of Al_2O_3 = 0.45) deposited on top of chemical oxide. The growth rate is linear for this composition and others in the range f= .04- 1, where f= the thickness fraction of Al_2O_3 in the nanolaminate. As shown in Figure 3, the deposition rate of the nanolaminates increases nearly linearly with increasing Al content from 0.42 A/pulse (f= 0.04) to 0.79 A/pulse (f= 0.96). All nanolaminate films show no incubation time for deposition on chemical oxide surfaces. This is a favorable attribute, which may indicate good nucleation behavior on these surfaces. In general, the optical interfacial thickness for the nanolaminates is about 10 A thicker than the pure metal oxides alone (i.e. Al_2O_3 & HfO_2). Figure 3 also shows interfacial optical thickness for the pure films and nanolaminates. There is roughly a 2-4 A increase in this thickness with the Al content of the film. The additional interfacial thickness of the nanolaminates compared to the pure films may be due to mixing of the layers to form a thicker nanolaminate-silicate layer.
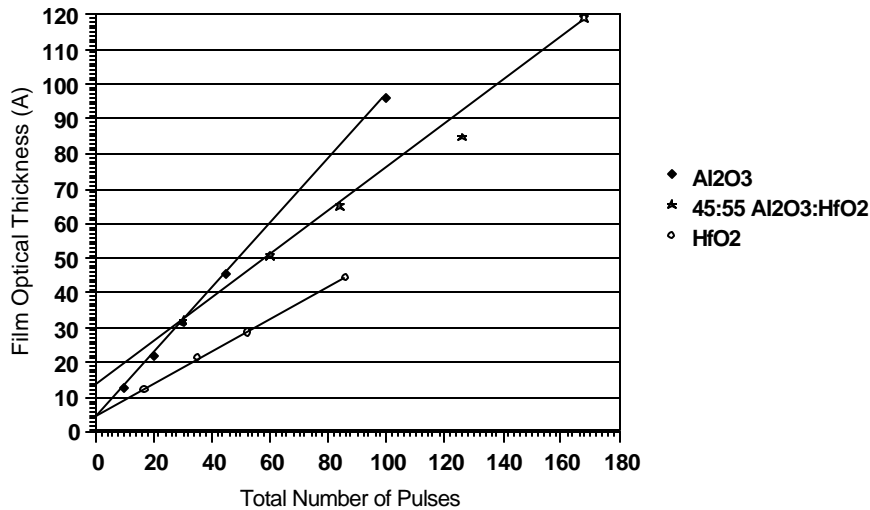

Figure 2: ALD high-K film nucleation on silicon. Films are deposited on top of chemical oxide.
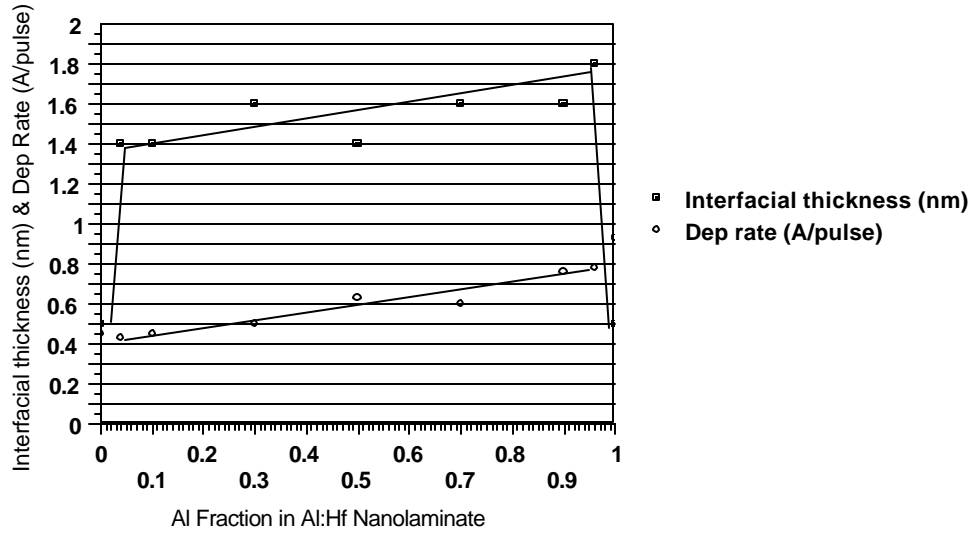
Figure 3: ALD nanolaminate film deposition rate (A/pulse) and interfacial thickness (measured by ellipsometry) vs. composition. High-K films are deposited on top of chemical oxide.

Figure 4 shows the deposition behavior of a typical nanolaminate (1:1 Al_2O_3:HfO_2) on various surface terminations. For a given number of pulses, the thickness of the nanolaminate grown on chemical, thermal oxide or oxynitrides is about 12 A thicker than the film grown on an HF-last treated silicon surface. There is no incubation time observed for deposition on any of the surfaces, indicating reasonable nucleation. The deposition rate on the different surfaces is the same, at least once the film grows thick enough to nucleate onto itself.

Growth curves of Al_2O_3 on HfO_2 surface and vice versa shows that the nucleation of one metal oxide on the other is faster than on an HF-last treated surface, but
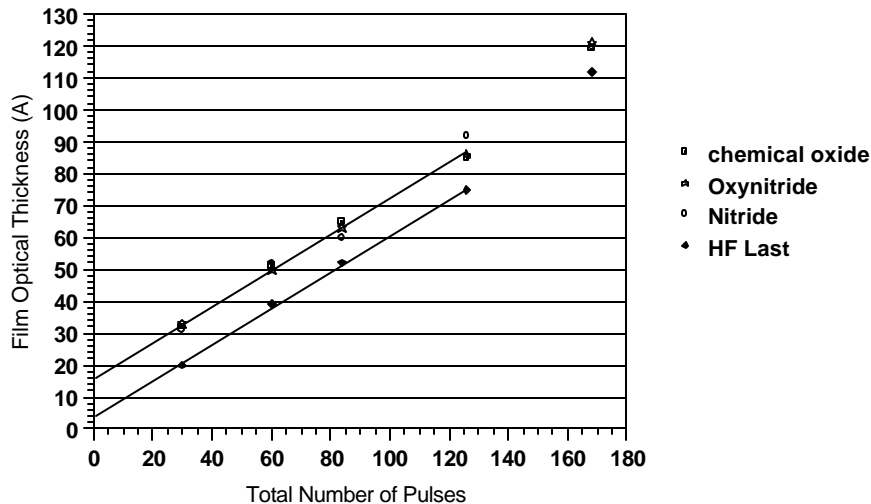

Figure 4: ALD nanolaminate film nucleation on different surface terminations. The nominal fraction of Al_2O_3 in Al: Hf nanolaminate = 0.45.

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slower than on chemical and thermal oxides or oxynitrides. For instance, deposition of Al_2O_3 on HfO_2 shows a 3 pulse incubation period compared to 5 pulse incubation on HF-last surfaces and no incubation on chemical or thermal oxides or oxynitrides.

Material Characterization: Refractive index, density, composition, morphology

The refractive index, film density, and composition of the nanolaminates were determined using spectral ellipsometry coupled with an X-ray source for accurate film thickness measurement. Figure 5 shows refractive index and film density vs. fraction of Al_2O_3 in the nanolaminate. The refractive index remains close to HfO_2 (fairly flat in the 1.9-2.1 range) for Al fractions from zero to about 0.75. After 0.75, the Nf drops rapidly toward that of pure Al_2O_3. Film density also decreases with increasing Al concentration, although the drop is less abrupt with concentration than refractive index.

In addition to spectral ellipsometry, MEIS was used to measure the stoichiometry of the nanolaminates. Figure 6 shows the experimental fraction of Al_2O_3 in the nanolaminates vs. nominal fraction, as calculated from the deposition rates of pure Al_2O_3 and HfO_2. Generally, the compositional data from MEIS and spectral ellipsometry are in close agreement with each other and the nominal composition. There is a slight discrepancy between the experimental and nominal composition for the mid-range, 50% composition. This may be due to the fact that there are only 2 pulses of HfO_2 and 1 pulse of Al_2O_3 used in the laminates repeating sequence. It may require more than 2 pulses of HfO_2 to form a uniform HfO_2 film on top of the Al_2O_3 surface.
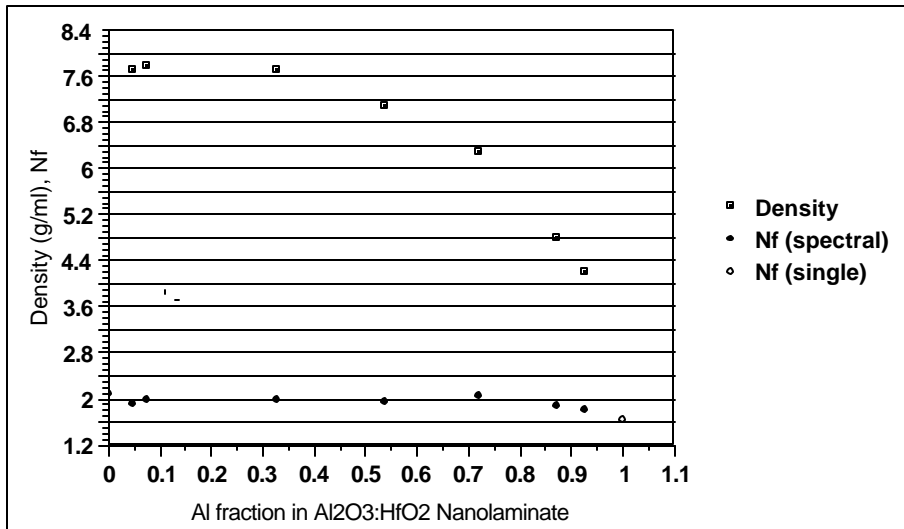

Figure 5: Film density and refractive index vs. composition for Al_2O_3:HfO_2 nanolaminates grown by ALD. Spectral ellipsometry was used to measure the density, Nf and composition on 50 A thick films.

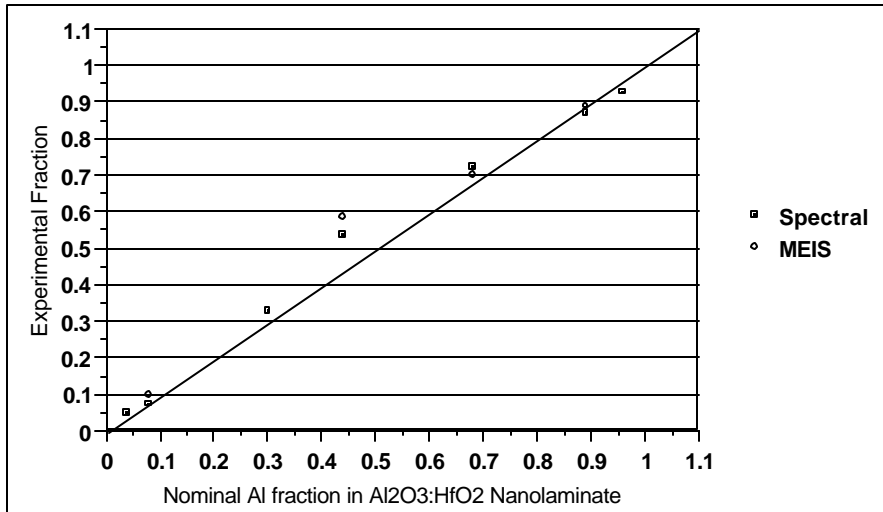Figure 6: Experimental Al_2O_3 fraction (determined by MEIS and spectral ellipsometry) vs. nominal fraction for the Al_2O_3:HfO_2 nanolaminates grown by ALD. Measurements were made on 50 A films.

Surface morphology was examined using TEM and AFM. TEM images of the nanolaminates, shown in Figure 7, show the 70% Al_2O_3 films to be amorphous as deposited, with smooth interfaces between the bottom interfacial layer and the polysilicon. After post annealing these films at 1000 C for 5 sec., the interfaces appear

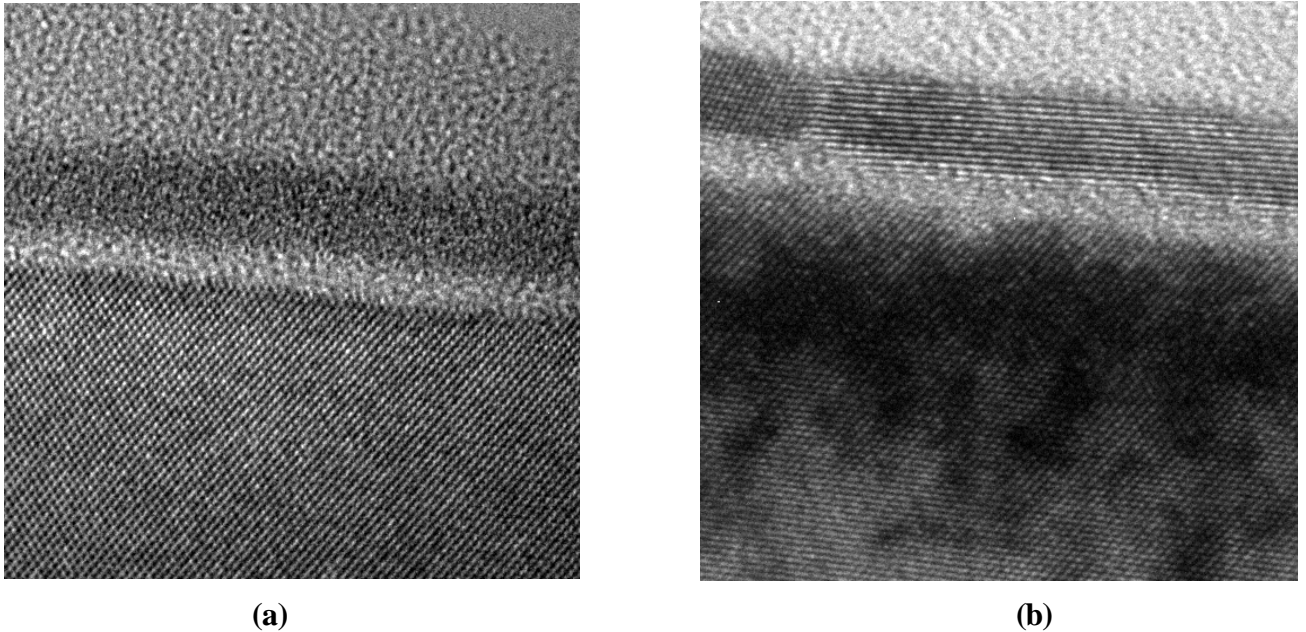(a)   (b)

Figure 7: TEM cross-section of 70 % Al_2O_3 in Al_2O_3:HfO_2 nanolaminate a) as deposited and b) after 1000 C, 5 sec. N2 anneal.

sharper and thicker, and there are some signs of crystallinity.

Surface roughness measurements of Al_2O_3 deposited on top of 20 A HfO_2 and HfO_2 deposited on top of 20 A Al_2O_3 were made using AFM. When depositing Al_2O_3 on top of HfO_2, the film remains amorphous and the rms and Rmax surface roughness do not increase from 10-100 pulses (about 8-80 A film thickness). When depositing HfO_2 on top of 20 A Al_2O_3, the film becomes more crystalline with increasing thickness and the increase in rms and Rmax surface roughness reflects this change. Table 1 below summarizes this data. For the nanolaminates, the number of pulses of Al_2O_3 and HfO_2 used in the repeating sequence is in most cases <10, with exception of 10% and 4% Al_2O_3 films. Thus, for most cases, the surface topology remains reasonably smooth throughout the growth, and the film remain amorphous.

Electrical Characterization of Nanolaminates:

The nanolaminates were electrically evaluated in polysilicon gate capacitor test structures. Al_2O_3 fractions of 0.1, 0.3, 0.5, 0.7 and 0.9 were tested. Electrical film thickness uniformity was found to be about 1.5 %, 1 sigma for equivalent oxide thicknesses (EOT) in the range of 15-20 A. The films non-uniformity is mostly derived from the HfO_2 part of the nanolaminate since HfO_2 ALD films (grown by $HfCl_4 + H_2O$) typically exhibit worse uniformity that Al_2O_3 ALD films ($Al(CH_3)_3 + H_2O$). The flatband shifts are excessive- ranging from 250-450 mV depending upon composition. The lowest flatband shift was observed for the 30% Al_2O_3 laminate (+263 mV).

Film	No. pulses	Thickness (A)	Rms (A)	Rmax (A)
Al2O3 on 20 A HfO2	10	8.2	1.06	12.44
Al2O3 on 20 A HfO2	30	24.6	1.03	16.65
Al2O3 on 20 A HfO2	100	82	1.11	11.15
HfO2 on 20 A Al2O3	17	8.3	1.58	16.94
HfO2 on 20 A Al2O3	52	25.48	1.49	15.09
HfO2 on 20 A Al2O3	172	84.3	1.96	30.94

Table 1: Surface roughness of different thicknesses of Al_2O_3 on HfO_2 surface and vice versa.

The gate leakage current of the nanolaminates is about 4-7 orders of magnitude lower than pure SiO_2, depending upon composition. Lowest leakage is seen for films in the 30-70% Al_2O_3 range. Figure 8 shows leakage current comparison of the nanolaminates to pure SiO_2, Al_2O_3 and HfO_2. The lowest leakage is seen for the 70% Al_2O_3 laminate. Charge trapping of the nanolaminates was also examined by measuring flatband shift as a function of voltage stress time. In general, the nanolaminates showed worse trapping than pure Al_2O_3 or HfO_2.
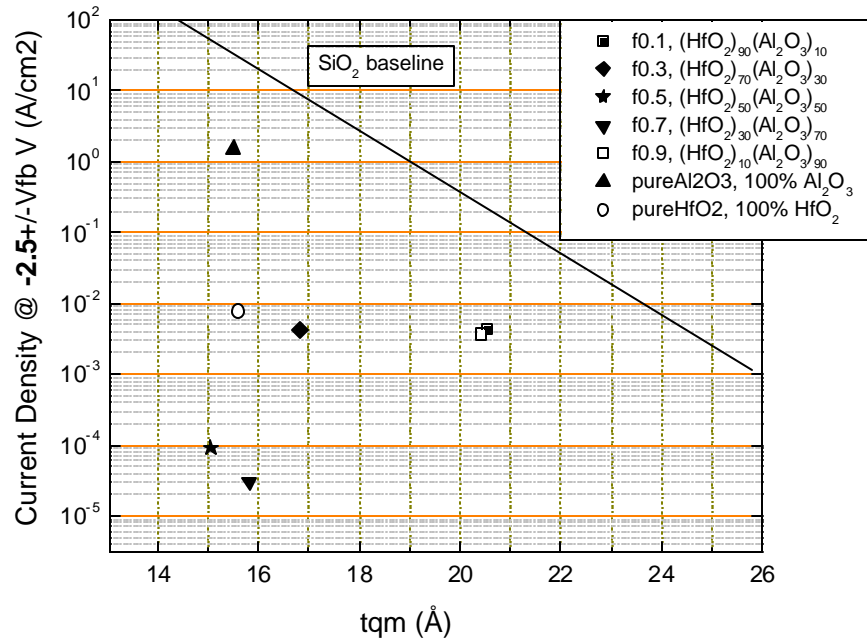
Figure 8: Leakage current density (at -2.5V + Vfb) vs. equivalent oxide thickess (EOT) for nanolaminates compared to SiO2

SUMMARY

ALD nanolaminates based on Al_2O_3 and HfO_2 offer a potential alternative as a gate dielectric candidate for advanced CMOS and memory devices. The advantages of these films include: good atomic layer control of film thickness and stoichiometry; good nucleation and smooth, amorphous films on chemical or thermal oxide or oxynitride layers; lower leakage current than SiO_2 (4-7 orders magnitude) or either Al_2O_3 or HfO_2 (1-3 orders of magnitude). The disadvantages of these films include: large flatband shifts (250-450 mV); C-V hysterisis, and excessive charge trapping for polysilicon gates.. Further work is needed to understand and overcome these disadvantages.

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1. nanolaminates   ………..

2. atomic layer deposition   ………..

3. gate dielectric

4. aluminum oxide……….

5. hafnium oxide.

6. high-k

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