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The Enhanced Dielectric and Insulating Properties of Al_2O_3 Modified Ta_2O_5 Thin Films

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Abstract. Future-generation memory devices will require materials with higher dielectric constants compared to conventional dielectric materials such as silicon oxide and silicon nitride. Tantalum oxide (Ta_2O_5) is one of the most promising high dielectric constant materials because of its ease of integration into conventional VLSI processes compared to other complex oxide dielectrics. The dielectric constant and thermal stability characteristics of bulk Ta_2O_5 samples were previously reported to enhance significantly through small substitutions of Al_2O_3. However, this improvement in the dielectric constant of $(1-x)Ta_2O_5$-xAl_2O_3 was not clearly understood. The present research attempts to explain the higher dielectric constant of $(1-x)Ta_2O_5$-xAl_2O_3 by fabricating thin films with enhanced dielectric properties. A higher dielectric constant of 42.8 was obtained for $0.9Ta_2O_5$-$0.1Al_2O_3$ thin films compared to that reported for pure Ta_2O_5 (25–30). This increase was shown to be closely related to a-axis orientation. Pure Ta_2O_5 thin films with similar a-axis orientation also exhibited a high dielectric constant of 51.7, thus confirming the orientation effect. Systematic study of dielectric and insulating properties of $(1-x)Ta_2O_5$-xAl_2O_3 thin films indicate improved leakage current properties and reliability characteristics such as temperature coefficient of capacitance and bias stability with increase in Al_2O_3 concentrations.

Keywords: tantalum oxide, dielectric, thin films

Introduction

The dielectric thin films find a variety of applications in VLSI circuits such as capacitor dielectrics, gate oxide, etching masks and for electrical isolation. For charge storage capacitor applications dielectric materials are required to posses high dielectric constant, low dielectric loss, low leakage currents, low defect density and high break down strength. These requirements are critical when the capacitors are used in microelectronic devices such as in dynamic random access memories (DRAM).

Dielectric materials that are currently used in DRAM capacitors are primarily based on silicon. Notables amongst these are SiO2 and Si_3N_4 with dielectric constants of 3.9 and 9.4 respectively. These materials posses excellent dielectric and insulating characteristics and also can be directly deposited onto silicon substrate. However, because of the low dielectric constant value of these materials, to achieve required charge storage density complex capacitor structures such as trench capacitors, stacked capacitors and crown shaped capacitors are currently being utilized. This approach has been pursued until the present generation of memory densities mainly because it allowed continued use of existing dielectric materials.

The development of future generation DRAMs (1 Gbit and beyond) will require introduction of new materials with higher dielectric constants in place of conventional nitride/oxide dielectrics [1]. Among a large number of candidate materials, Ta_2O_5 is considered one of the most promising [2]. The advantages of Ta_2O_5 are it's simpler processing and compatibility with the existing semiconductor processing technology. However only a moderately high dielectric

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constant value of Ta_2O_5 ($\varepsilon_r \sim 25$) compared to the conventional dielectrics is a significant limitation for it's practical application.

It was recently reported that for 'bulk Ta_2O_5' addition of small amounts of Al_2O_3 significantly improves the dielectric constant and it's thermal stability [3]. However, no physical understanding for the observed improvement in the dielectric constant was established. Furthermore, the effects on leakage current characteristics, a major obstacle in the use of Ta_2O_5 in high-density integrated circuits were not reported. To exploit these enhanced properties in microelectronic applications, thin films with properties comparable to bulk need to be fabricated. Earlier we have demonstrated the feasibility of depositing $(1-x)Ta_2O_5$-$xAl_2O_3, x = 0.1$ ('x' is weight fraction) thin films with enhanced dielectric properties similar to what was observed in bulk materials [4–5]. In this paper we attempt to provide an understanding of the observed enhancement in dielectric properties due to Al_2O_3 addition and also present a systematic study of structural, surface morphological and electrical properties of Al_2O_3 modified Ta_2O_5 thin films. The dielectric and insulating characteristics were studied at different film compositions, processing temperature and at different test conditions such as ambient temperature, applied bias and operating frequency.

Fabrication Procedure

Modified Ta_2O_5 films were prepared using metallorganic solution decomposition (MOSD) technique. The substrate used was platinum coated Si (100) which hitherto will be referred as Pt substrate. A room temperature chemical solution preparation method was developed using tantalum ethoxide and aluminum nitrate as precursors and 2-methoxyethanol and acetic acid as solvents respectively. Steps involved in the preparation of Al_2O_3 modified Ta_2O_5 thin films are shown in the Fig. 1. Initially a desired amount (estimated from desired film composition) of Aluminum nitrate [$Al(NO_3)_3 \cdot 9H_2O$] was weighed and dissolved in 5 ml of acetic acid [CH_3COOH]. Another solution of tantalum ethoxide [$Ta(OC_2H_5)_5$] in 15 ml of 2-methoxy ethanol was prepared separately. Both these solutions were mixed and diluted with 2-metoxy ethanol to lower solution viscosity and to permit uniform deposition on a spin coater. This mixture was stirred for 2 hours at room temperature and only then used for spin coating.

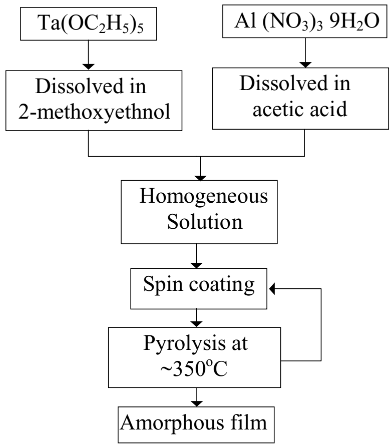

Fig. 1. Flow chart for the preparation of modified Ta_2O_5 thin films by metallorganic solution decomposition (MOSD) technique.

Spin coating was carried out by placing Pt substrates on a rotating platform and covering it with the precursor solution and rotating at 6000 rpm for 60 seconds. Immediately after the deposition, the film was transferred onto a hot surface maintained at 350°C. This step was to remove the solvents present in the newly formed film and also to carry out the pyrolysis process. This process was repeated until approximately 0.2 μm thin films were deposited.

The deposited films were annealed at different temperatures in the temperature range of 600°C–800°C. Annealing processes was carried out in a conventional tube furnace and samples were introduced in to a pre-heated furnace. Continuous flow of O_2 was maintained during the annealing process. The dielectric and insulating properties were measured in metal/insulator/metal configuration. Circular dots (Area $= 3.4 \times 10^{-4}$ cm^2) of Pt were sputter deposited on the film as top electrode. Dielectric constant was calculated by measuring the capacitance between the top Pt dot and the substrate. The leakage currents were measured on the same structure by applying *dc* bias across the top and bottom electrodes.

The crystal structure and the phase formation of the thin films were analyzed using a Scintag XDS 2000 difractometer (Cu Kα radiation at 40 kV). The film thickness and optical properties were measured using a variable angle spectroscopic ellipsometry. The dielectric properties were measured between 10 kHz and 1 MHz using HP4192A impedance analyzer. The

C-V measurements were conducted by applying a small ac signal of 10 mV amplitude and 100 kHz frequency across the sample while the dc electric field was swept from a positive bias to negative bias and back again. The leakage current characteristics were measured using HP4140B test system by applying dc voltages with a step height of 1 V and a delay time of 30 s.

Results and Discussion

Physical Properties of xAl_2O_3-$(1 - x)$ Ta_2O_5 Thin Films

The X-ray difractometry (XRD) studies were performed on modified Ta_2O_5 thin films to examine the phase formation, crystal structure and the crystallization temperature. Figure 2 shows a comparison of the X-ray diffraction patterns of $0.9Ta_2O_5$-$0.1Al_2O_3$ and Ta_2O_5 thin films. The XRD patterns revealed that the thin films are polycrystalline with no evidence of any secondary phases. Crystalline phase of the thin films was identified by comparing the X-ray diffraction peaks of the thin films with those of the standards (JCPDS 25-922). The phase of crystallized modified Ta_2O_5 thin films was identified as a low temperature β-Ta_2O_5 modification. The crystallization temperature was strongly dependent on the film composition that increased with increasing Al_2O_3 composition as summarized in Table 1. It was observed that as-deposited thin films, irrespective of their composition were amorphous. The surface morphology of the modified Ta_2O_5 thin films was observed by atomic force microscopy (AFM). Micrograph of the 1 μm × 1 μm scan area of a $0.9Ta_2O_5$-$0.1Al_2O_3$ sample is shown in the Fig. 3. The average surface roughness values were observed to be less than 0.3 nm. These films exhibited a dense microstructure with a very fine grain size.

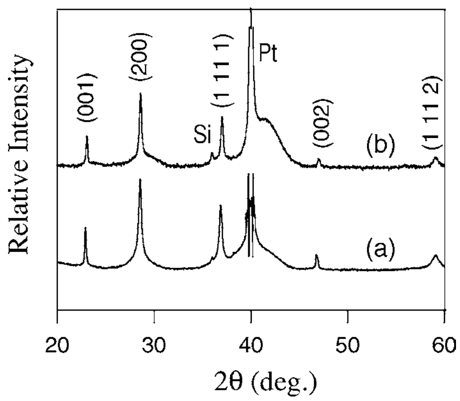

Fig. 2. X-ray diffraction patterns of (a) Pure Ta_2O_5 thin and (b) $0.9Ta_2O_5$-$0.1Al_2O_3$ thin film.

Table 1. Crystallization temperature of $(1 - x)Ta_2O_5$-xAl_2O_3 thin films as a function of film composition

x (%)	Crystallization temperature (°C)
0	>600°C
5	>650°C
10	>700°C
15	>750°C
20	>750°C

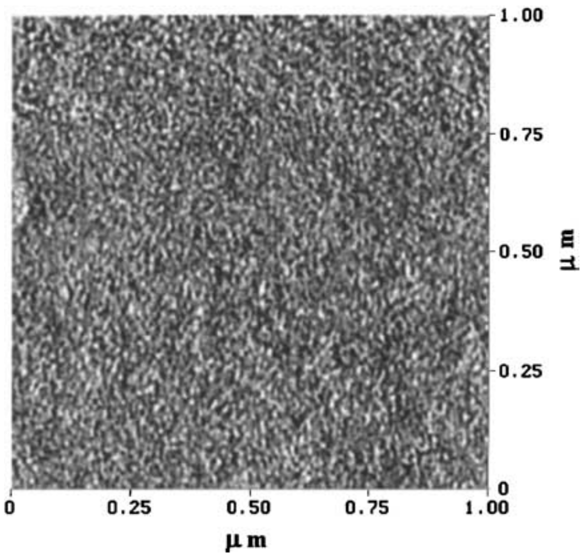

Fig. 3. Surface morphology of $0.9Ta_2O_5$-$0.1Al_2O_3$ thin films as observed by Atomic Force microscopy (AFM) micrograph.

Dielectric and Insulating Properties

The dielectric properties of $(1 - x)Ta_2O_5$-xAl_2O_3 thin films were measured in terms of dielectric constant and dissipation factor. The small signal dielectric constant and the dissipation factor for a $0.9Ta_2O_5$-$0.1Al_2O_3$ thin film annealed at 750°C were 42.8 and 0.005 respectively. This dielectric constant value is much improved compared to the typically reported value of around 25 for pure Ta_2O_5 thin films. Figure 4 shows the small signal dielectric constant and dissipation factor as a

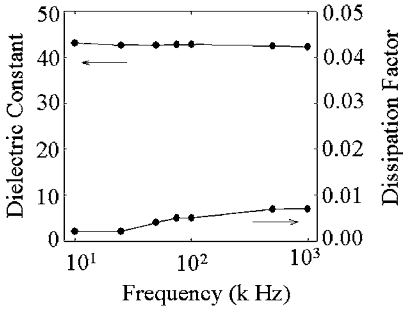

Fig. 4. A plot of dielectric constant and dissipation factor with frequency for $0.9Ta_2O_5$-$0.1Al_2O_3$ thin films.

function of frequency. Negligible dispersion in dielectric properties up to 1 MHz indicates the absence of any surface layer or electrode barrier effects in capacitance measurements. The enhancement of dielectric constant of $0.9Ta_2O_5$-$0.1Al_2O_3$ is consistent with the values reported for bulk material by R.J. Cava et al.

A physical understanding of the factors contributing to the high dielectric constant of the $0.9Ta_2O_5$-$0.1Al_2O_3$ thin films is important to exploit the enhanced properties in devices. In order to explain the observed enhancement, a correlation between the Ta_2O_5 crystal structure and the dielectric constant was investigated.

The dielectric and piezoelectric properties of Ta_2O_5 have been observed to exhibit a strong directional anisotropy with significantly high dielectric constant in the a-axis direction compared to other directions [6–8]. The X-ray diffraction pattern of $0.9Ta_2O_5$-$0.1Al_2O_3$ thin films with dielectric constant of 40.8 is shown in the Fig. 2. A strong (200) oriented peak can be observed from the figure suggesting a preferred a-axis orientation in the films. Figure 5 compares XRD patterns of $0.9Ta_2O_5$-$0.1Al_2O_3$ thin film with bulk samples (dielectric constant of ∼25). It can be observed that (200) peak for bulk sample is much weaker relative to other peaks. Note that if high dielectric constant of $0.9Ta_2O_5$-$0.1Al_2O_3$ thin films is due to the effect of a-axis orientation, then preferentially oriented pure Ta_2O_5 thin films are also expected exhibit high dielectric constant. Studies were conducted on Ta_2O_5 thin films to verify this structure-property correlation. The processing and post-deposition annealing conditions were optimized to get crystalline Ta_2O_5 thin films with strong a-axis orientation as was obtained in the case of $0.9Ta_2O_5$-$0.1Al_2O_3$ thin films. The pure Ta_2O_5

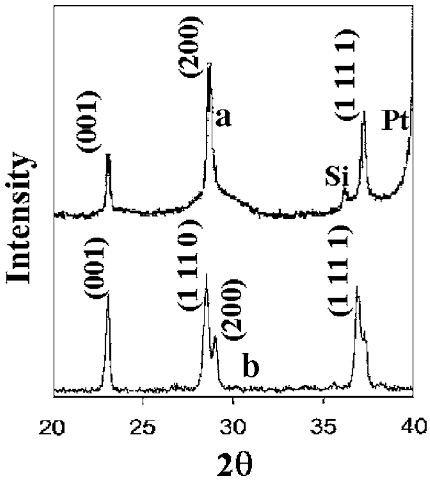

Fig. 5. Comparison of XRD patterns of (a) $0.9Ta_2O_5$-$0.1Al_2O_3$ thin (b) Ta_2O_5 bulk samples.

thin films also exhibited a well-crystallized orthorhombic phase with strong (200) orientation, as shown in the Fig. 2. The dielectric measurements on Ta_2O_5 thin films showed a small signal dielectric constant of 51.7 and loss factor of 0.008 at a measuring frequency of 100 kHz.

The above observations suggest strong correlation between the high dielectric constant of modified Ta_2O_5 and preferred *a*-axis orientation in the films. Table 2 summarizes the dielectric properties of modified Ta_2O_5 thin films at different film compositions. It can be observed from the table that the dielectric constants of the amorphous thin films are generally lower in the range of 21–27 and those of crystallized films are in the range of 40.8–41.7. The high dielectric constant of 51.7 for pure Ta_2O_5 thin films with strong *a*-axis orientation suggests that a dielectric constant of 42.8

Table 2. Summary of the dielectric properties of Al_2O_3 modified Ta_2O_5 thin films

	T_A = 700 (°C)		T_A = 750 (°C)		T_A = 800 (°C)	
x	ε_r	tan(δ)	ε_r	tan(δ)	ε_r	tan(δ)
0	51.7	0.008				
0.05	39.7	0.011	40.8	0.007		
0.10	24.8*	0.009	42.5	0.004		
0.15	24.0*	0.007	27.0*	0.007	40.6	0.009
0.20	21.0*	0.006	25.0*	0.006	44.6	0.005

'*' refers to films in amorphous phase.

Table 3. Leakage current density of $(1-x)Ta_2O_5$-xAl_2O_3 thin films: Annealing temperature of the sample is in parenthesis

	I_L (A/cm^2) at 1 MV/cm	
x	Amorphous	Crystalline
0	2.1×10^{-10} (<600°C)	4.5×10^{-7} (>650°C)
0.05	3.0×10^{-10} (<650°C)	5.9×10^{-8} (>700°C)
0.10	2.0×10^{-10} (<700°C)	3.4×10^{-8} (>750°C)
0.15	3.2×10^{-10} (<700°C)	3.0×10^{-8} (>800°C)
0.20	7.2×10^{-10} (<700°C)	4.3×10^{-9} (>800°C)

for $0.9Ta_2O_5$-$0.1Al_2O_3$ thin films is not an improvement compared to a-axis oriented Ta_2O_5 value. Even though the Al_2O_3 modified Ta_2O_5 thin films showed a lower dielectric constant than pure Ta_2O_5 thin films, the dielectric loss, leakage currents and reliability characteristics were found to be significantly improved as compared to Ta_2O_5. The loss factor of these thin films was found to be lower than the values reported for Ta_2O_5 films fabricated by other deposition techniques [9–13].

Low leakage current is another important requirement for a good DRAM capacitor. Otherwise, the stored charge in the capacitor leaks off with time through various mechanisms, which necessitates frequent refreshing leading to higher power consumption. Measurements on modified Ta_2O_5 thin films indicate significant improvement in this respect with Al_2O_3 addition. Systematic study on the effects of Al_2O_3 in Ta_2O_5 is summarized in Table 3. It was noted that for both pure and modified Ta_2O_5 thin films conductivity did not exhibit any appreciable change with the polarity, indicating the formation good interfaces at the bottom and top electrodes. It can be observed from the Table 3 that the leakage currents in amorphous thin films are significantly lower than those for crystalline thin films. Among the crystallized films, leakage currents decreased with the increase in Al_2O_3 in the film composition. For $0.8Ta_2O_5$-$0.2Al_2O_3$ films leakage currents were approximately an order of magnitude lower than those for pure Ta_2O_5 films.

Reliability Characteristics of Al_2O_3 modified Ta_2O_5 Thin Films

One of figure of merits for a capacitor's is its temperature coefficient of capacitance (TCC). The TCC

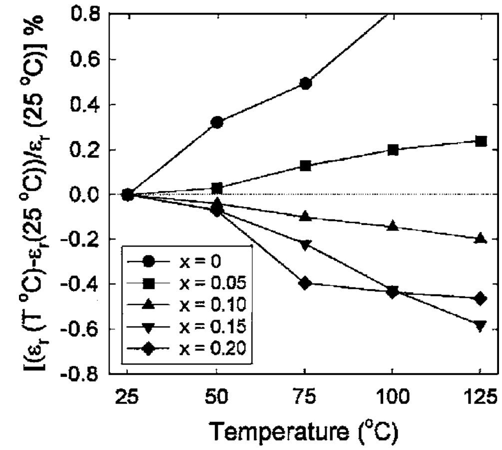

Fig. 6. Temperature dependence of dielectric properties of $(1-x)$ Ta_2O_5-xAl_2O_3 thin films.

is defined in terms of a parameter $\Delta C/C_o$ where ΔC is the change in capacitance relative to the capacitance C_o at 25°C. The TCC of modified Ta_2O_5 thin film capacitors was analyzed in the temperature range of 25°C to 125°C. Figure 6 shows a plot of normalized capacitance vs. ambient temperature for modified Ta_2O_5 thin films. Pure Ta_2O_5 thin films were found to exhibit a positive TCC of 112 ppm/°C. Increase in Al_2O_3 composition was found to decrease TCC eventually resulting in a negative TCC for $0.8Ta_2O_5$-$0.2Al_2O_3$. These observations on thin films are in good agreement with the reported values for bulk ceramic Ta_2O_5.

Additionally, modified Ta_2O_5 thin film capacitors were subjected to *dc* electric fields up to 1 MV/cm and the change of the capacitance was measured. These measurements are summarized in the Table 4. It can be observed that modified Ta_2O_5 thin films exhibited improved bias stability compared to the pure

Table 4. Bias stability of the capacitance of crystalline $(1-x)Ta_2O_5$-xAl_2O_3 thin films

x	Bias stability of capacitance (0 to 1 MV/cm) (%)
0	1.41
0.05	0.76
0.10	0.40
0.15	0.23
0.20	0.24

Ta_2O_5 thin films. The bias stability of pure Ta_2O_5 was found to be 1.41% and it decreased to 0.23% for $0.8Ta_2O_5$-$0.2Al_2O_3$ sample. A large variation in dielectric constant with the frequency may also indicate presence of ferroelectric phase in the film [14]. A plot of dielectric constant and dielectric loss versus frequency for a $0.9Ta_2O_5$-$0.1Al_2O_3$ is shown in the Fig. 4. Modified Ta_2O_5 films exhibited negligible dependence on frequency of operation up to 1 MHz.

Conclusions

The Al_2O_3 modified Ta_2O_5 thin films exhibited improved dielectric and insulating characteristics compared to those of pure Ta_2O_5 thin films. An enhanced dielectric constant in the range of 39–47 was obtained for these films. Investigation on the structural properties indicated that the thin films exhibited a preferred orientation in the (200) direction. Leakage current densities of modified Ta_2O_5 thin films were found to be up to an order of magnitude lower than the pure Ta_2O_5 thin films. Thermal stability and the bias stability of the modified Ta_2O_5 thin films were dependent on composition suggesting that these dielectrics can be tailored to suit specific applications. Improved dielectric and insulating properties and the compatability of Ta and Al in semiconductor processing suggest that the modified Ta_2O_5 is a promising material for dielectric applications.

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