Structural and electrical properties of crystalline (1x) Ta 2 O 5 –x Al 2 O 3 thin films fabricated by metalorganic solution deposition technique

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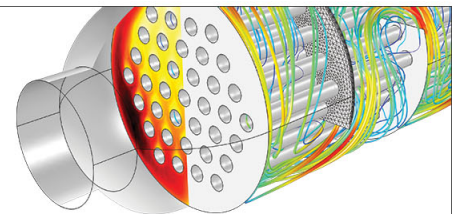
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Polycrystalline $(1-x)\text{Ta}_2\text{O}_5-x\text{Al}_2\text{O}_3$ thin films were fabricated by metalorganic solution deposition technique on Pt-coated Si substrate at a temperature of 750 °C. Thin films with $0.9\text{Ta}_2\text{O}_5-0.1\text{Al}_2\text{O}_3$ composition exhibited improved dielectric and insulating properties compared to Ta_2O_5 thin films. The measured small signal dielectric constant and dissipation factor at 100 kHz were 42.8 and 0.005, respectively. The temperature coefficient of capacitance was 20 ppm/°C in the measured temperature range of 25–125 °C. The leakage current density was lower than 6×10^{-8} A/cm^2 up to an applied electric field of 1 MV/cm. A charge storage density of 18.9 fC/μm^2 was obtained at an applied electric field of 0.5 MV/cm. The high dielectric constant, low dielectric loss, low leakage current density, and good temperature and bias stability suggest $(1-x)\text{Ta}_2\text{O}_5-x\text{Al}_2\text{O}_3$ thin films to be a suitable dielectric layer in integrated electronic devices in place of conventional dielectrics such as SiO_2 or Si_3N_4. © *1997 American Institute of Physics.* [S0003-6951(97)03736-4]

Ta_2O_5 is a promising material for applications in high density dynamic random access memories (DRAMs), electroluminescent display devices, and gate dielectrics of metal-oxide-semiconductor devices due to its high dielectric constant, low leakage current, low defect density, and high breakdown field strength.[1–5] Ta_2O_5 is a suitable alternative to conventional insulator materials like Si_3N_4 and SiO_2 in very large scale integrated technology. The high dielectric constant and low loss insulating materials are also attractive for microwave devices.[6] For successful integration into these electronic devices, extremely reliable Ta_2O_5 films with high temperature and field stability are desired. The properties of Ta_2O_5 films have been reported to be strongly dependent on the fabrication method, nature of substrate and electrode material, and postdeposition annealing treatment.[7,8] Ta_2O_5 based composites have been investigated to improve the dielectric and insulating properties of tantalum oxide.[3,9] Recently, it was shown that the electrical properties of bulk Ta_2O_5 can be significantly improved through 10% substitution of Al_2O_3.[10] The present work is an effort to fabricate the thin films of $(1-x)\text{Ta}_2\text{O}_5-x\text{Al}_2\text{O}_3$ material with enhanced dielectric and insulating properties compared Ta_2O_5 for microelectronic applications. The $(1-x)\text{Ta}_2\text{O}_5-x\text{Al}_2\text{O}_3$ material is expected to be compatible with semiconductor processing where both Ta and Al are already in use.

In this letter, we report the fabrication of the $(1-x)\text{Ta}_2\text{O}_5-x\text{Al}_2\text{O}_3$ thin films by metalorganic solution deposition (MOSD) technique. MOSD processing has been extensively used in thin film technology because of easier composition control, good homogeneity, and uniform deposition over a large substrate surface area.[11] Thin films of $(1-x)\text{Ta}_2\text{O}_5-x\text{Al}_2\text{O}_3$ were fabricated using aluminum nitrate and tantalum ethoxide as precursors. Acetic acid and 2-methoxyethanol were selected as solvents. In the experiment, aluminum nitrate was initially dissolved in acetic acid. The clear solution thus formed was diluted with

2-methoxyethanol and then the solution of tantalum ethoxide in 2-methoxyethanol was added to it with constant stirring. The viscosity of the solution was controlled by varying the 2-methoxyethanol content. The precursor films were coated on to Pt-coated Si substrates by spin coating using a photoresist spinner operated at 6000 rpm for 60 s. Particulates were removed from the solution by filtering through 0.2 μm syringe filters. After spinning onto various substrates, films were kept on a hot plate in air for 10 min. After each coating, this step was repeated to ensure complete removal of volatile matter. The postdeposition annealing of the films was carried out in an oxygen atmosphere. In the present letter, we report the structural and electrical properties of 0.3 μm thick films with $0.9\text{Ta}_2\text{O}_5-0.1\text{Al}_2\text{O}_3$ composition as the bulk material with the same composition exhibited the best dielectric and insulating properties. The crystallinity of the films was examined by x-ray diffraction (XRD). The microstructure of the films was analyzed by atomic force microscopy (AFM). The electrical properties reported include dielectric, current–voltage $(I-V)$ and capacitance–voltage $(C-V)$.

The pyrolyzed films (at ~350 °C) were found to be amorphous and postdeposition annealing was required to develop crystallinity. The structure of the films was analyzed by Scintag XDS 2000 diffractometer using Cu $K\alpha$ radiation at 40 kV. Figure 1 shows the XRD pattern of the films annealed at 750 °C. The films annealed at 700 °C were found to be amorphous in nature. As the annealing temperature was increased to 750 °C, the films were found to be well crystallized with peaks attributable to orthorhombic ($\beta-\text{Ta}_2\text{O}_5$) phase. The XRD patterns revealed that the films were polycrystalline in nature with no evidence of preferred orientation or secondary phases. The surface morphology of the $0.9\text{Ta}_2\text{O}_5-0.1\text{Al}_2\text{O}_3$ thin films was analyzed by Digital Instrument's Dimension 3000 atomic force microscope using tapping mode with amplitude modulation. The scan area was 1×1 μm. The surface morphology of the films was smooth with no cracks and defects, as shown in Fig. 2, and the average surface roughness was less than 0.3 nm. The films
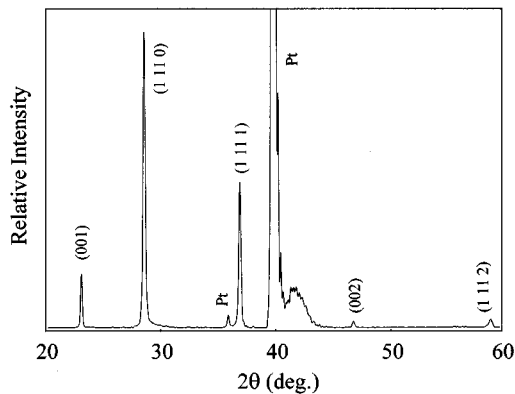
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FIG. 1. X-ray diffraction patterns of $0.9Ta_2O_5-0.1Al_2O_3$ thin films annealed at 750 °C.

FIG. 3. Dielectric constant and dissipation factor of 0.3 μm thick $0.9Ta_2O_5-0.1Al_2O_3$ films as a function of frequency.

exhibited a dense microstructure and the grain size was very fine.

The dielectric properties of $0.9Ta_2O_5-0.1Al_2O_3$ thin films were measured in terms of the dielectric constant ϵ_r and loss factor tan δ. The dielectric measurements were conducted on metal-insulator-metal (MIM) capacitors with a HP 4192A impedance analyzer. Several platinum electrodes (area$=3.7\times10^{-4}$ cm^2) were sputter deposited through a shadow mask on the top surface of the films to form MIM capacitors. Figure 3 shows the low field dielectric constant and dissipation factor as a function of frequency for a 0.3 μm thick film annealed at 750 °C. The small signal dielectric constant and dissipation factor at a frequency of 100 kHz were 42.8 and 0.005, respectively. The dielectric constant for $0.9Ta_2O_5-0.1Al_2O_3$ thin films was found to be much improved compared to the typical value ($\epsilon_r\sim25-30$) reported for Ta_2O_5 thin films. The loss factor was found to be much lower than values reported for Ta_2O_5 thin films fabricated by various techniques.[8,12–15] The permittivity showed no dispersion with frequency up to about 1 MHz, as shown in Fig. 3, indicating that the values were not masked by any surface layer effects or electrode barrier effects. As the frequency was increased above 1 MHz, the dielectric constant was found to decrease and the loss factor was found to increase with frequency. This behavior was found to be extrinsic in nature as similar behavior was observed at around the same
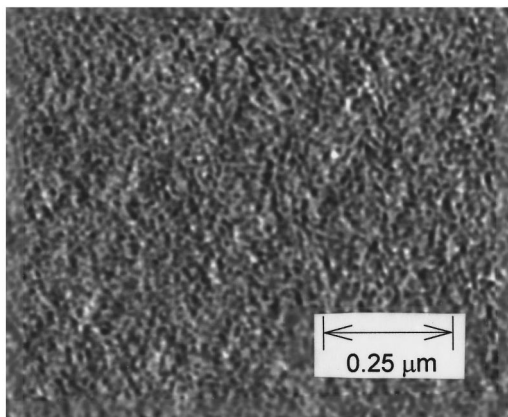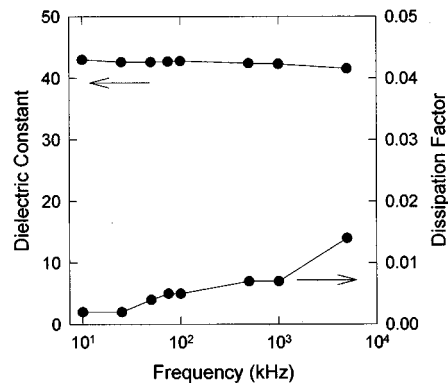
frequency for thin films of other dielectric materials.[16] At frequencies of the order of a few MHz, the stray inductance L of the contacts and wires and/or the presence of a finite resistance in series with the films, which may arise due to intrinsic or extrinsic sources, may cause such behavior.[17] Figure 4 shows the dependence of the film capacitance and the loss factor on the measurement temperature in the range 25–125 °C. The temperature stability of the capacitance was measured in terms of the parameter $\Delta C/C_0$, where ΔC is the change in capacitance relative to the capacitance C_0 at 25 °C. The change in film capacitance relative to film capacitance at 25 °C was found to be lower than 0.2% up to 125 °C indicating good temperature stability of $0.9Ta_2O_5-0.1Al_2O_3$ capacitors. The loss factor was found to increase from 0.005 to 0.012 as the temperature was increased from 25 to 125 °C. The temperature coefficient of capacitance in the measured temperature range of 25–125 °C was found to be 20 ppm/°C which is comparable to the value reported for bulk material. The high dielectric constant, low dielectric loss, and good thermal stability characteristics show the suitability of $0.9Ta_2O_5-0.1Al_2O_3$ thin films as the insulating dielectric layer for large value capacitors for various electronic devices.

For DRAM applications, a material with high dielectric constant and good insulating characteristics is required. A limiting factor for any DRAM capacitor dielectric is leakage current. In a DRAM cell, the stored charge on the capacitor leaks off with time through various leakage mechanisms
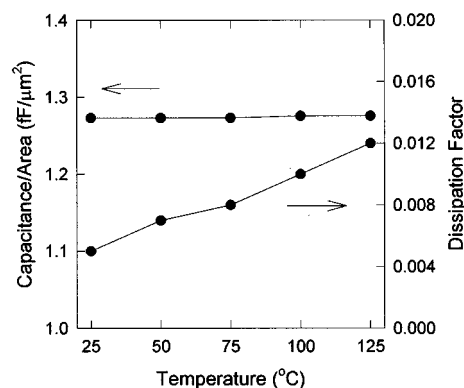

FIG. 2. AFM photograph of $0.9Ta_2O_5-0.1Al_2O_3$ thin films annealed at 750 °C.

FIG. 4. Dielectric constant and dissipation factor of 0.3 μm thick $0.9Ta_2O_5-0.1Al_2O_3$ films as a function of measurement temperature.
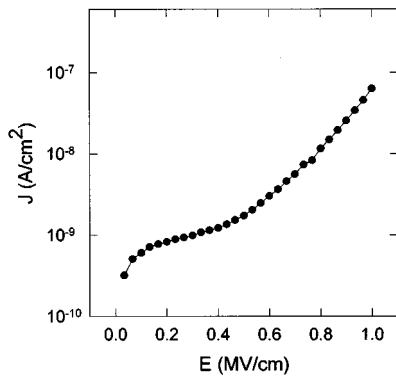
FIG. 5. $J-E$ characteristics of 0.3 μm thick $0.9Ta_2O_5$–$0.1Al_2O_3$ films annealed at 750 °C.

which requires periodic refreshing of the stored charge. So the leakage current characteristics of the storage capacitor dielectric are very important for DRAM applications. Figure 5 shows the leakage current characteristics of $0.9Ta_2O_5$–$0.1Al_2O_3$ thin films. The leakage current density versus electric field characteristics, as shown in Fig. 5, were measured using HP 4140B test system by applying dc voltages with a step height of 1 V and a delay time of 30 s. The film conductivity was not found to change appreciably with change in the polarity of the applied voltage indicating bulk limited conduction process. The leakage current density of the films was lower than 6×10^{-8} A/cm^2 up to an applied electric field of 1 MV/cm indicating good insulating characteristics. The leakage current density was found to be much improved compared to Ta_2O_5 thin films reported by various techniques.[5,7,8,12–15,18]

The $C-V$ measurements were conducted on MIM capacitors to analyze the bias stability. Figure 6 shows the $C-V$ curves of Pt/$0.9Ta_2O_5$–$0.1Al_2O_3$/Pt capacitors obtained by applying a small ac signal of 10 mV amplitude and of 100 kHz frequency across the capacitor while the dc electric field was swept from a negative bias to positive bias. The change in film capacitance was found to be less than 0.4% up to an applied voltage of 20 V indicating good field stability. The loss factor also showed good bias stability, as shown in Fig. 6, and was found to vary in the range 0.005–0.007. The charge storage density, defined by $Q_c = \epsilon_0 \epsilon_r E$, was also measured from $C-V$ characteristics. Here, ϵ_0 is the permit-
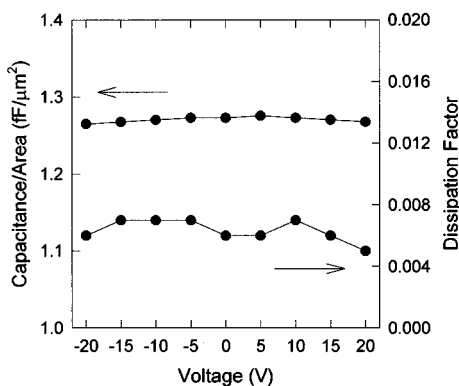
tivity of free space, ϵ_r is the dielectric constant of the film, and E is the applied electric field. The charge storage density was calculated to be 18.9 fC/μm^2 at an applied electric field of 0.5 MV/cm. At this bias the leakage current density was lower than 10^{-9} A/cm^2. The high charge storage density compared to conventional dielectrics and low leakage current density suggest the suitability of $0.9Ta_2O_5$–$0.1Al_2O_3$ thin films for DRAM applications.

In conclusion, thin films of $0.9Ta_2O_5$–$0.1Al_2O_3$ with crystalline structure were successfully prepared by metalorganic solution deposition technique on Pt-coated Si substrates. For thin films with $0.9Ta_2O_5$–$0.1Al_2O_3$ composition, the dielectric and the insulating properties were found to be much improved compared to Ta_2O_5 thin films. The measured small signal dielectric constant and dissipation factor at 100 kHz were 42.8 and 0.005, respectively. The MIM capacitors exhibited good temperature and bias stability. The temperature coefficient of capacitance was 20 ppm/°C in the measured temperature range of 25–125 °C. The leakage current density was lower than 6×10^{-8} A/cm^2 up to an applied electric field of 1 MV/cm. A charge storage density of 18.9 fC/μm^2 was obtained at an applied electric field of 0.5 MV/cm. The compatibility of Ta and Al with semiconductor processing, and good dielectric and leakage current characteristics suggest the suitability of $(1-x)Ta_2O_5$–xAl_2O_3 thin films as capacitor dielectric layer for microelectronic applications.

FIG. 6. $C-V$ characteristics of 0.3 μm thick $0.9Ta_2O_5$–$0.1Al_2O_3$ films annealed at 750 °C.

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