Influence of Postdeposition Annealing on the Enhanced Structural and Electrical Properties of Amorphous and Crystalline Ta$_2$O$_5$ Thin Films for Dynamic Random Access Memory Applications

by P. C. Joshi and M. W. Cole

ARL-RP-24

June 2001


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Tantalum oxide (Ta$_2$O$_5$) thin films were fabricated on Pt-coated Si, n+ Si, and poly-Si substrates by metalorganic solution deposition technique. The effects of postdeposition annealing on the structural, electrical, and optical properties were analyzed. The Ta$_2$O$_5$ films were amorphous up to 600 °C. A well-crystallized orthorhombic phase with strong a-axis orientation was obtained at an annealing temperature of 650 °C. The refractive index was found to increase with annealing temperature and a value of 2.08 (at 630 nm) was obtained for films annealed at 750 °C. The electrical measurements were conducted on metal-insulator-metal (MIM) and metal-insulator-semiconductor capacitors. The dielectric constant of amorphous Ta$_2$O$_5$ thin films was in the range 29.2–29.5 up to 600 °C, while crystalline thin films, annealed in the temperature range 650–750 °C, exhibited enhanced dielectric constant in the range 45.6–51.7. The high dielectric constant in crystalline thin films was attributed to orientation dependence of the dielectric permittivity. The dielectric loss factor did not show any appreciable dependence on the annealing temperature and was in the range 0.006–0.009. The frequency dispersion of the dielectric properties was also analyzed. The films exhibited high resistivities of the order $10^{12}$ – $10^{13}$ Ω cm at an applied electric field of 1 MV/cm in the annealing temperature range of 500–750 °C. The measurement of current-voltage (I-V) characteristics in MIM capacitors indicated the conduction process to be bulk limited. The I-V characteristics were ohmic at low fields, and Poole-Frenkel effect dominated at high fields. The temperature coefficient of capacitance was in the range 52–114 ppm/°C for films annealed in the temperature range 500–750 °C. The bias stability of capacitance, measured at an applied electric field of 1 MV/cm, was better than 1.41% for Ta$_2$O$_5$ films annealed up to 750 °C. For a 0.15-μm-thick film, a unit area capacitance of 3.0 fF/μm$^2$ and a charge storage density of 22.3 fC/μm$^2$ were obtained at an applied electric field of 0.5 MV/cm.
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(Received 5 March 1999; accepted for publication 16 April 1999)

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I. INTRODUCTION

The development of future generation of dynamic random access memories (DRAMs) will require the introduction of new materials with higher dielectric constant than the conventional SiO$_2$ or silicon oxide/nitride based systems. As the supply voltages of DRAMs and available area for the capacitor decrease rapidly, the thickness of the dielectric has to be decreased considerably to maintain similar charge storage densities. However, the conventional dielectric thickness has reached a lower limit set by electron tunneling through the dielectric. The use of high dielectric constant material will make it possible to achieve similar charge storage density as conventional dielectrics at relatively larger thicknesses and lead to the design of planar or nearly planar capacitor geometry and can significantly improve yield when compared to deep trench or stack capacitor designs. Among the dielectric materials under investigation, Ta$_2$O$_5$ is one of the most promising insulator materials for DRAM cell capacitors. Tantalum oxide thin films are attractive for scaled down capacitor in ultralarge scale integrated (ULSI) circuits because of their high dielectric constant, low dielectric loss, low leakage current, low defect density, and good temperature and bias stability. The high dielectric constant and low dielectric loss materials are also attractive for microwave applications. Ta$_2$O$_5$ thin films have potential for numerous microelectronic applications such as gate dielectric of metal--insulator--semiconductor (MIS) devices, optical waveguides, electroluminescent display devices, and surface acoustic wave (SAW) devices.

For successful integration into microelectronic devices, extremely reliable Ta$_2$O$_5$ thin films are desired. Several thin film growth techniques such as anodization, thermal oxidation, electron-beam evaporation, reactive sputtering, excimer-laser assisted chemical vapor deposition, metalorganic chemical vapor deposition (MOCVD), ultraviolet photo chemical vapor deposition (photo-CVD), low-pressure chemical vapor deposition (LPCVD), plasma-enhanced chemical vapor deposition (PECVD) have been employed to fabricate good quality Ta$_2$O$_5$ thin films. The properties of Ta$_2$O$_5$ thin films have been reported to be strongly dependent on the fabrication method, nature of substrate and electrode material, and post-
II. EXPERIMENT

Ta_{2}O_{5} thin films were fabricated by MOSD technique using tantalum ethoxide \([\text{Ta(OC}_{2}\text{H}_{5})_{3}]\) as precursor. 2-methoxyethanol \((\text{H}_{5}\text{COCH}_{2}\text{CH}_{2}0\text{H})\) was used as solvent. Figure 1 shows the general steps in the fabrication of Ta_{2}O_{5} thin films by MOSD technique. In the experiment, tantalum ethoxide was initially dissolved in 2-methoxyethanol. Finally, acetic acid \((\text{CH}_{3}\text{COOH})\) was added to prevent rapid hydrolysis and precipitation of the metal oxide. The viscosity and surface tension of the solution was adjusted by varying the 2-methoxyethanol content. The precursor films were coated onto various substrates by spin coating using photo-resist spinner. Dust and other suspended impurities were removed from the solution by filtering through 0.2 \(\mu\text{m}\) syringe filter. The thickness of the films was controlled by adjusting the viscosity of the solution and spin speed. Pt-coated Si, n^{-}-Si, and poly-Si substrates were used in the study. Prior to the deposition of the films, the silicon substrates were cleaned by a room-temperature technique entitled spin etching\(^{18}\) to remove the native silicon oxide and make the substrate surface hydrogen terminated. After spinning onto various substrates, films were kept on a hot plate (at \(\sim 350^\circ\text{C}\)) in air for 10 min to remove solvents and other organic. This step was repeated after each coating to ensure complete removal of volatile matter. The postdeposition annealing of the films was carried out in a furnace at various temperatures in an oxygen atmosphere. The structure of the films was analyzed by x-ray diffraction (XRD). The XRD patterns were recorded on a Scintag XDS 2000 diffractometer using Cu \(K\alpha\) radiation at 40 kV. The surface morphology of the films was examined by Digital Instrument's Dimension 3000 atomic force microscope (AFM) using tapping mode with amplitude modulation. The sample thickness and optical properties were measured by variable angle spectroscopic ellipsometry using Woollam VB-200 ellipsometer. The electrical measurements were conducted on films in MIM and MIS configurations. Several platinum electrodes were sputter deposited through a shadow mask on the top surface of the films to form MIM and MIS capacitors. Capacitance and \(\tan \delta\) values were measured by HP4192A LF impedance analyzer. The capacitance–voltage \((C-V)\) characteristics were also measured with HP4192A. The insulating properties and dominant conduction mechanism in amorphous and crystalline Ta_{2}O_{5} thin films were analyzed through the measurements of leakage current versus voltage \((J-V)\) characteristics in MIM capacitors using HP4140B semiconductor test system.

III. RESULTS AND DISCUSSION

A. Structure and morphology

The as-pyrolyzed films (at \(\sim 350^\circ\text{C}\)) films were amorphous in nature, and postdeposition annealing was required to impart crystallinity. The postdeposition annealing of the films was carried out in the temperature range 500–750°C in an oxygen atmosphere. Figure 2 shows the XRD patterns of the Ta_{2}O_{5} thin films deposited on Pt-coated Si substrates as a function of annealing temperature. All the films were 0.15 \(\mu\text{m}\) thick and annealed for 60 min. The absence of diffraction peaks in XRD patterns of films annealed up to 600°C indicated that these films were amorphous. It was possible to obtain a well-crystallized phase at an annealing temperature of 650°C with no evidence of secondary phases. As the annealing temperature was increased, the peak intensity in XRD patterns increased and the full width at half maximum (FWHM) decreased, indicating enhanced crystallinity and an increase in grain size with increasing annealing temperature.
The presence of intense diffraction peak corresponding to (200) plane and the relatively weaker diffraction from (001) and (002) planes implied that the deposited Ta₂O₅ thin films possessed a strong preferential orientation. Similar trends were observed in the XRD patterns of Ta₂O₅ thin films deposited on silicon substrates (n+ and poly) by the MOD technique indicating preferential orientation. The lattice constants a, b, and c, calculated using (001), (200), and (111) peaks in the XRD pattern, were 6.225, 39.8521, and 3.8609 Å, respectively. These values were in good agreement with those reported for bulk Ta₂O₅, suggesting that the films were crystallized in the orthorhombic phase.

The surface morphology of Ta₂O₅ thin films was analyzed by AFM using tapping mode with amplitude modulation. The scan area was 1×1 μm². The surface morphology of the films was smooth, as shown in Fig. 3, with no cracks and defects. The films exhibited a dense microstructure and fine grain size. The average surface roughness was found to increase with increase in annealing temperature with average surface roughness value of 4 nm at 750 °C. There was no appreciable effect of the annealing temperature on the microstructure of amorphous Ta₂O₅ thin films, while crystalline films showed an increase in grain size with increasing annealing temperature which is consistent with the XRD studies indicating an increase in peak sharpness with annealing temperature. Larger grain sizes are expected with increasing annealing temperature because of amorphous to crystalline phase transformation and increase in surface mobility, thus allowing the films to decrease its total energy by growing larger grains and decreasing its grain boundary area.

B. Dielectric and optical properties

The dielectric properties of Ta₂O₅ thin films were measured in terms of the dielectric constant ε, and loss tangent tan δ. The small signal dielectric measurements were conducted on MIM and MIS capacitors by applying an alternating current (ac) signal of 10 mV amplitude. The effects of applied frequency, film thickness, and postdeposition annealing temperature on the dielectric properties were also analyzed. Figure 4 shows the low field dielectric constant and dissipation factor of 0.15-μm-thick Ta₂O₅ film, annealed at 750 °C, as a function of frequency. The small signal dielectric constant and dissipation factor at a frequency of 100 kHz were 51.7 and 0.008, respectively. The permittivity showed no appreciable dispersion with frequency up to about 1 MHz, as shown in Fig. 4, indicating that the values were not masked by any surface layer effects or electrode barrier effects in this frequency range. The dielectric constant was found to decrease slightly with frequency as the frequency
TABLE I. Effects of postdeposition annealing temperature on the dielectric and optical properties of Ta$_2$O$_5$ thin films.

<table>
<thead>
<tr>
<th>$T_a$ (°C)</th>
<th>$\varepsilon_r$</th>
<th>$\tan \delta$</th>
<th>$\alpha$</th>
<th>$\eta$</th>
<th>TCK (ppm/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>29.2</td>
<td>0.007</td>
<td>1.98</td>
<td>+51</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>29.5</td>
<td>0.009</td>
<td>2.01</td>
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<td></td>
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<tr>
<td>650</td>
<td>45.6</td>
<td>0.009</td>
<td>2.05</td>
<td>+66</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>50.4</td>
<td>0.007</td>
<td>2.06</td>
<td>+77</td>
<td></td>
</tr>
<tr>
<td>750</td>
<td>51.7</td>
<td>0.008</td>
<td>2.08</td>
<td>+114</td>
<td></td>
</tr>
</tbody>
</table>

The dielectric constant and the dissipation factors were in the range 45.6–51.7 and 0.006–0.009, respectively, for films annealed in the temperature range 650–750 °C. The increase in the dielectric constant of the crystalline thin films with annealing temperature may be attributed to improved crystallinity and increase in grain sizes and density of the films as indicated by XRD and AFM studies.

There is a wide variation in the reported dielectric constant of amorphous and crystalline Ta$_2$O$_5$ thin films. The dielectric constant of amorphous and crystalline thin films has been reported in the range (14–31)$^{11,18,23–29}$ and (24–60)$^{23,26,28–30}$ respectively. The dielectric properties of thin films strongly depend on the fabrication method, nature of substrate and electrode material, postdeposition annealing treatment, crystallographic orientation, microstructure, thickness of samples, and film–substrate interface characteristics.

was increased above 1 MHz. At around the same frequency, the dissipation factor showed a rapid increase in value with frequency. For any dielectric material, the intrinsic frequency dependence of the material or the effects due to electrodes or any internal interfacial barrier may induce such a resonance. Presence of an appreciable resistance, which may be arising from intrinsic or extrinsic sources, in series with the dielectric film can affect the dielectric response at high frequencies. Similar frequency dispersion behavior due to finite resistance of the external electrodes has been reported for other dielectric materials.$^{20}$ In the present study, the resonance behavior was found to be extrinsic in nature as similar resonance was observed at around the same frequency for thin films of other dielectric materials having similar order of capacitance.$^{11,22}$ The observed resonance behavior for amorphous and crystalline Ta$_2$O$_5$ thin films was found to be dependent on the film capacitance and shifted towards lower frequencies for larger capacitances indicating that the source of resonance was extrinsic in nature. At the frequencies of the order of a few megahertz, the stray inductance $L$ of the contacts and wires may induce an $L-C$ resonance at a resonant frequency, $f_r$, given by

$$f_r = \frac{1}{2\pi \sqrt{LC}}$$

where $C$ is the capacitance of the sample under test. For thin films having capacitance of the order of 1 nF or so, a stray inductance of the order of a few micro-Henries can induce $L-C$ resonance in the megahertz frequency range. As the resonance behavior was observed at a frequency higher than 1 MHz, all the dielectric measurements were conducted at frequencies much lower than this resonance frequency. At these frequencies, the internal accuracy of the impedance analyzer was always better than 1%.

Table I shows the effect of postdeposition annealing temperature on the dielectric properties of Ta$_2$O$_5$ thin films. There was no appreciable effect of the annealing temperature on the dielectric properties as long as the films were in amorphous state. The dielectric constant and the dissipation factor for amorphous Ta$_2$O$_5$ thin films were in the range 29.2–29.5 and 0.006–0.009, respectively, up to an annealing temperature of 600 °C. The dielectric constant was found to increase to 45.6 at an annealing temperature of 650 °C as the films were well crystallized. The dielectric constant of crystalline Ta$_2$O$_5$ thin films was found to increase with increase in annealing temperature while the loss factor did not show any appreciable dependence on the annealing temperature. The
and dielectric constant and a comparison was made with the value reported for bulk material. The calculated value of $\alpha_2$, 19.63 Å$^2$, was in good agreement with the reported value for bulk Ta$_2$O$_5$ suggesting that the high dielectric constant in the present crystalline Ta$_2$O$_5$ thin films was due to strong a-axis orientation which was also evident in XRD studies. This structural dependence of the dielectric properties and the wide variation in the values reported in the literature strongly emphasize the need to correlate the structural properties of thin films with their dielectric properties.

In order to analyze size effects on the dielectric properties, the dielectric measurements were conducted on Ta$_2$O$_5$ thin films as a function of film thickness. Figure 5 shows the variation of low field dielectric constant and dissipation factor of Ta$_2$O$_5$ thin films annealed at 700 °C as a function of dielectric film thickness. The dielectric constant and the dissipation factor did not show any appreciable dependence on film thickness in the range 36–260 nm. At smaller thicknesses the dielectric constant was found to decrease with film thickness while the loss tangent was found to increase. The measured dielectric constant and loss factor were in the range 43.2–50.4 and 0.008–0.022, respectively, for 17–260 nm-thick films. Similar thickness dependence of the dielectric properties has been reported by others for very thin films. Similar thickness dependence includes stress in the films and the existence of barrier layer near one or both the electrodes. The stress resulting from the difference in the thermal expansion coefficient of the film and the substrate and that from the structure and growth of the films, which are usually found to have thickness dependence, may contribute to the thickness dependence of the dielectric constant. The dielectric film thickness effects on the properties are dominant in thin films when the grain size is larger than or of the order of film thickness. Under these conditions, the thickness dependence of the grain size contributes to the thickness dependence of the dielectric properties. However, the possibility of surface layer effects at lower thicknesses may not be ignored. The effect of dielectric film thickness on the charge storage capacity was also investigated. For planar capacitors, the charge storage capacity is defined by $C_{storage} = \epsilon_0 \epsilon_r A / d$. In conventional downscaling of physical dimensions of very large scale integrated devices, one has to reduce the area of the capacitor proportionally. Additionally, one reduces the thickness of the dielectric layer by the scaling factor, in order to achieve required capacitance density. In DRAM techniques, the attempt is to retain high $C_{storage}$ by optimizing these capacitor parameters. Ta$_2$O$_5$ can offer an order of magnitude higher capacitance density, at relatively larger thicknesses, in a DRAM cell capacitor compared to other conventional gate dielectrics such as SiO$_2$. Figure 6 shows the capacitance per unit area of Ta$_2$O$_5$ thin films as a function of film thickness. The unit area capacitance of a 17-nm-thick film was 22.5 fF/µm$^2$. It is equivalent to a SiO$_2$, a conventional gate dielectric, thickness of 1.6 nm. The high charge storage capacitance per unit area of Ta$_2$O$_5$ thin films even at smaller thicknesses shows their potential for high density DRAMs and integrated capacitor applications.

The effects of substrate on the dielectric properties were analyzed by measurement of dielectric properties on MIM and MIS capacitors. The MIS capacitor is the most commonly used active component for silicon ULSI circuits. The device technology has been hindered by the very high density of states at the interface of Si and insulator. A poor interface of dielectric film with silicon leads to high leakage currents, higher frequency dispersion, and high defect trapped charges. Several attempts have been made to improve the effective dielectric constant and leakage current characteristics of Ta$_2$O$_5$ based MIS capacitors by optimizing the fabrication techniques and/or postdeposition annealing treatment. In the present case, the Ta$_2$O$_5$ thin films were deposited on $n$-Si and poly-Si substrates to analyze the effects of Ta$_2$O$_5$ film–silicon interface on the dielectric properties. Table II shows the effect of substrate on the dielectric properties of amorphous and crystalline Ta$_2$O$_5$ thin films. The dielectric properties of Ta$_2$O$_5$ thin films deposited on $n$-Si and poly-Si substrates were compared with those deposited on Pt-coated Si substrates to analyze the effects of
compared to films deposited on Pt-coated Si substrates due to the growth of interfacial oxide layer on silicon substrates. There was no significant difference in the dielectric constant of thin films deposited on various substrates indicating the absence of any appreciable oxide thickness at film–substrate interface. The films annealed at 750 °C showed much lower dielectric constant on silicon substrates as compared to films deposited on Pt-coated Si substrates indicating the presence of an appreciable oxide growth at the interface. The thickness of the oxide layer was calculated by comparing the dielectric constant of MM and MIS capacitors by assuming the formation of a uniform oxide layer between the film and substrate with no interdiffusion. The thickness of the silicon oxide layer was calculated from the relation, $1/C^2_\text{fr}=1/C^2_f+1/C^2_\text{SiO}_2$, by considering the total capacitance ($C_T$) of the MIS capacitor to be a series combination of $\text{Ta}_2\text{O}_5$ film capacitance ($C_f$) and $\text{SiO}_2$ layer capacitance ($C_\text{SiO}_2$). For the present $\text{Ta}_2\text{O}_5$ thin films the thickness of the silicon oxide layer was found to be less than 2.5 nm on both $n^+$-Si and poly-Si substrates indicating that the combination of spin etching and MOSD technique were effective in minimizing the film–substrate interface reaction and providing good interfacial properties. Low temperature processing is essential to obtain good film/Si interfacial characteristics. Annealing temperature effects up to 1000 °C have been analyzed for $\text{Ta}_2\text{O}_5$ thin films in an attempt to improve their electrical properties. Annealing at high temperatures severely degrades the film/Si interface and requires close control of processing parameters to improve the electrical properties. Low temperature processing is necessary to minimize interfacial reactions and integrate $\text{Ta}_2\text{O}_5$ thin films into semiconductor devices.

The temperature and bias stability of the dielectric properties of $\text{Ta}_2\text{O}_5$ thin films were also analyzed to establish their reliability for integrated electronic applications. Figure 7 shows the dielectric constant and dissipation factor of crystalline $\text{Ta}_2\text{O}_5$ thin film annealed at 750 °C as a function of measurement temperature. The dielectric constant and the dissipation factor were relatively unchanged with measurement temperature in the range 25–125 °C indicating good temperature stability of the present $\text{Ta}_2\text{O}_5$ thin films. The temperature coefficient of capacitance (TCK) was calculated for the present films using the equation, $\Delta C/(C_0\Delta T)$ where $\Delta C$ is the change in capacitance relative to capacitance $C_0$ at 25 °C and $\Delta T$ is the change in temperature relative to 25 °C.

Table I shows the temperature coefficient of capacitance of $\text{Ta}_2\text{O}_5$ thin films, measured in the temperature range 25–125 °C, as a function of annealing temperature. The films showed a low TCK of +52 ppm/°C up to an annealing temperature of 600 °C. The TCK for the crystalline films, as shown in Table I, was found to be higher than that of amorphous films. Crystalline $\text{Ta}_2\text{O}_5$ thin films annealed at 750 °C exhibited a low TCK of +114 ppm/°C establishing good reliability of present $\text{Ta}_2\text{O}_5$ thin films for integrated capacitor applications. The low temperature coefficient of capacitance for the present films indicates completeness of oxidation and low defect concentration in amorphous and crystalline $\text{Ta}_2\text{O}_5$ thin prepared by MOSD technique.

The optical properties of $\text{Ta}_2\text{O}_5$ thin films were determined by ellipsometry. The experimentally determined psi and delta values were transformed into refractive index by assuming an optical model consisting of single homogeneous nonabsorbing film on Pt-coated Si substrates. The refractive index and the band-gap values were found to be 2.08 (at 630 nm) and 5.11 eV, respectively, for a 0.15-μm-thick film annealed at 750 °C. The refractive index value is comparable to that reported for crystalline $\text{Ta}_2\text{O}_5$ thin films prepared by MOCVD, reactive sputtering, and LPCVD techniques. The effects of postdeposition annealing temperature on the refractive index were also analyzed. The refractive index value was found to increase with the increase in annealing temperature, as shown in Table I, which may be attributed to change in microstructure of the films from amorphous to crystalline, and increase in crystallinity and density of the films. There is a considerable variation in the reported refractive index of amorphous (1.70–2.18) and crystalline (1.74–2.32) $\text{Ta}_2\text{O}_5$ thin films. The refractive index of thin films strongly depends on impurities, imperfection, and voids in the films, which are incorporated during growth process. The combined effect of crystal structure, voids, imperfection, film–substrate interactions, processing conditions, etc., may be responsible for the wide variation in the reported refractive index values of $\text{Ta}_2\text{O}_5$ thin films. It is difficult to com-

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$\varepsilon_0$</th>
<th>tan $\delta_0$</th>
<th>$\varepsilon_f$</th>
<th>tan $\delta_f$</th>
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<tbody>
<tr>
<td>$n^+$-Si</td>
<td>28.5</td>
<td>0.018</td>
<td>43.7</td>
<td>0.018</td>
</tr>
<tr>
<td>poly-Si</td>
<td>29.0</td>
<td>0.008</td>
<td>45.7</td>
<td>0.010</td>
</tr>
<tr>
<td>Pt-coated Si</td>
<td>29.5</td>
<td>0.008</td>
<td>51.7</td>
<td>0.008</td>
</tr>
</tbody>
</table>

TABLE II. Effect of substrate on the dielectric properties of $\text{Ta}_2\text{O}_5$ based MIM and MIS capacitors.
pare the data of different workers unless porosity and oxygen content of the film are known.

C. Capacitance–voltage (C–V) characteristics

The C–V measurements were conducted on MIM capacitors to analyze the bias stability. Figure 8 shows the C–V curves of Pt/Ta₂O₅/Pt capacitors obtained by applying a small ac signal of 10 mV amplitude and of 100 kHz frequency across the capacitor, while the direct current (dc) electric field was swept from a negative bias to positive bias. There was no appreciable change in the capacitance of amorphous Ta₂O₅ thin films up to an applied electric field of 1 MV/cm indicating good bias stability. It was possible to measure the change in film capacitance for crystalline thin films. The change in the film capacitance was found to be 1.41% for crystalline Ta₂O₅ thin films, annealed at 750 °C, at an applied electric field of 1 MV/cm. The loss factor also showed good bias stability, as shown in Fig. 8, and was less than 1% up to 1 MV/cm.

A DRAM cell needs a film with high charge storage density and low leakage current density. The charge storage density, defined by $Q_c = \varepsilon_0 \varepsilon_r E$, was calculated based on the information from C–V measurements on MIM capacitors. Here, $E$ is the applied electric field. Figure 9 shows the relation between the charge storage density and the applied electric field for a 0.15-µm-thick film. The charge storage density was 22.3 fC/µm² at an applied electric field of 0.5 MV/cm. At this bias the leakage current density was lower than $10^{-8}$ A/cm². The high charge storage density compared to conventional dielectrics and low leakage current density suggest the suitability of present Ta₂O₅ thin films for integrated capacitor applications.

D. Leakage current characteristics

Leakage current is one of the limiting factors for the suitability of a dielectric material for DRAM applications. In a DRAM cell, the stored charge on a capacitor leaks off with time through various leakage mechanisms, and a periodic refreshing is required to maintain the charge above a threshold for reliable operation. Thus, the leakage current characteristics of the storage capacitor dielectric are very important in a DRAM cell. The leakage current characteristics of Ta₂O₅ thin films were measured using MIM capacitors by applying dc voltages with a step delay time of 30 s. A delay of 30 s after applying the voltage gave current readings close to the ones measured after much longer waiting times. Figure 10 shows the leakage current density versus electric field characteristics of 0.15-µm-thick films as a function of annealing temperature. The leakage current density showed a strong dependence on the postdeposition annealing temperature and was considerably higher for crystalline thin films as compared to amorphous thin films. The resistivity of amorphous thin films was found to be of the order of $10^{12} \Omega$ cm, as shown in Table III, while that of crystalline thin films was of the order of $10^{10} \Omega$ cm at an applied electric field of 1 MV/cm. The high resistivity observed in the present films was attributed to the low oxygen content and high porosity of the films.
TABLE III. Effect of postdeposition annealing temperature on the resistiv-
ing, high frequency dielectric permittivity \( \varepsilon_{\text{ao}} \), and parameter \( \alpha \) of 0.15-\( \mu \)m-
thick \( \text{PbTa}_2\text{O}_5\)-Pt capacitors.

<table>
<thead>
<tr>
<th>( T_A (\degree \text{C}) )</th>
<th>Resistivity (1 cm) ( (\text{at 1 MV/cm}) )</th>
<th>( \varepsilon_{\text{ao}} )</th>
<th>( \varepsilon_{\text{elec}} = \varepsilon_{\text{ao}} )</th>
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</thead>
<tbody>
<tr>
<td>500</td>
<td>( 6 \times 10^4 )</td>
<td>3.92</td>
<td>1.20</td>
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<td>600</td>
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<td>700</td>
<td>( 3 \times 10^5 )</td>
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<td>750</td>
<td>( 2 \times 10^5 )</td>
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shows the completeness of phase formation and oxidation of \( \text{Ta}_2\text{O}_5 \) thin films prepared by MOSD technique. In the amorphous phase the leakage current density was found to decrease with the increase in temperature, while crystalline thin films showed an increase in leakage current with annealing temperature. Several reports exist in literature showing an increase in leakage current density of \( \text{Ta}_2\text{O}_5 \) thin films as a result of crystallization. \(^{10,23,25,28}\) Most of these reports focus on the properties of \( \text{Ta}_2\text{O}_5 \) thin films deposited on Si substrates. The increase in leakage current density has been attributed to various factors such as oxygen vacancy, impurity (carbon/hydrocarbon) content, presence of incompletely oxidized silicon at the grain boundaries near film/substrate interface. In this study the leakage current characteristics of \( \text{Ta}_2\text{O}_5 \) thin films were analyzed in MIM configuration, so no interfacial effects were expected in the annealing temperature range of 500–750 \( \degree \text{C} \) to contribute to the observed leakage current behavior. The leakage current of thin film strongly depends on the various material related parameters such as composition, structure, impurities, homogeneity, stress, and local effects (compositional variations, dopant segregation, grain boundaries, pores, high defect density, etc.). The structural imperfections and stress strongly influence the electrical properties of amorphous thin films. The decrease in the leakage current density of amorphous \( \text{Ta}_2\text{O}_5 \) thin films can be attributed to the decrease in defect density, compressive stress, and increase in oxidation with increasing annealing temperature. The coordination number of oxygen atoms to Ta atoms has been reported to increase with increase in annealing temperature for LPCVD deposited \( \text{Ta}_2\text{O}_5 \) thin films. \(^{25}\) The reduction in stress and defect density, which are found to be annealing temperature dependent, will lead to an improvement in leakage current characteristics.

The steady state field dependent dc conductivity was examined by the measurement of \( I-V \) characteristics in MIM capacitors. Several electrical processes allow electrical charges to move in insulators, leading to sizeable current densities, especially when the insulating film is thin (typically less than 1 \( \mu \)m). For thin insulating films of the order of 1 \( \mu \)m, if an appreciable voltage can be sustained (of the order of few volts), the field strength is of the order of \( 10^2 \) V/cm and greater. The low field properties are usually ohmic in nature, that is, current \( I \) is linear with voltage \( V \). At high fields these films exhibit nonlinear \( I-V \) relationship. Generally, the high field characteristics cannot be adequately described by a single conduction process; usually the different field strength ranges manifest different electrical phenomena.

An understanding of the mechanisms of nonlinear conductivity in thin insulators is pertinent to the development of thin film devices for microelectronics. In general, the leakage current in an insulator is either controlled by the film–electrode interface or bulk of the insulator. The \( I-V \) characteristics of the present \( \text{Ta}_2\text{O}_5 \) thin films were found to be ohmic at low fields and highly nonlinear, as shown in Fig. 10, at high fields. The leakage current characteristics showed thickness dependence even at low applied voltages indicating bulk limited current conduction. \(^{46}\) There was no change in the magnitude of conductivity with change in the polarity of the applied voltage, which also indicated the conduction process to be bulk limited and not electrode limited. These films exhibited high resistivities in the range \( 10^{12} \Omega \cdot \text{cm} \). In this range of resistivities, the possible dominant conduction mechanisms may be (a) tunneling, (b) Poole–Frenkel effect, and/or (c) space-charge-limited conduction. As the thickness of the films was well above 50 nm, the tunneling process was ruled out. Poole–Frenkel effect is the flow of trapped charge carriers in insulators through lowering of potential barrier in the bulk of the insulator due to applied electric field. The barrier arises due to the Coulombic potentials surrounding ionized sites in the film. The electrons having enough energy to transit over the energy barrier contribute to the current. The current density–electric field \( (J-E) \) relation for Poole–Frenkel flow is given by the equation\(^{47}\)

\[ J = AE \exp \left( -\frac{q \phi_0}{k_B T} \right) \exp \left( \frac{\beta_{\text{PF}}}{\alpha k_B T} E^{1/2} \right) \]

with

\[ \beta_{\text{PF}} = \left( \frac{q^2}{\pi \varepsilon_0 \varepsilon} \right)^{1/2}, \]

where \( A \) is a constant, \( \phi_0 \) is the metal–insulator barrier height, \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature, \( \alpha \) is a parameter, \( 1 \leq \alpha \leq 2 \), which takes into account the trapping sites in insulator, \( \beta_{\text{PF}} \) is the Poole–Frenkel constant, \( q \) is the electronic charge, \( \varepsilon_0 \) is the permittivity of free
The parameter $\alpha$ is equal to 1 for a trap free insulator, while the value is between 1 and 2, indicating a trap-modulated conduction process, depending on the location of the Fermi level. Figure 11 shows the $\ln(J/E) = E^{-1/2}$ plot for Ta$_2$O$_5$ thin film. The straight line behavior of this plot at high fields indicated the Poole–Frenkel flow to be the dominant conduction mechanism. Similar straight line behavior was observed in the high field regime of $\ln(J/E) = E^{-1/2}$ plots for both amorphous and crystalline thin films annealed in the temperature range 500–750°C indicating that the nonohmic conduction in Ta$_2$O$_5$ thin films was due to Poole–Frenkel flow. However, the onset of this high field regime was found to be shifted to lower fields, from 1.4 to 0.6 MV/cm, with increase in annealing temperature from 500 to 700°C. The slope of the straight line region in $\ln(J/E) = E^{-1/2}$ plots at high fields is given by the expression

$$\text{slope} = \frac{d \ln(J/E)}{dE^{-1/2}} = \frac{\beta_{PF}}{\alpha kT}.$$

The value of the coefficient $\beta_{PF}$ was calculated from the slope of the straight line region. The high frequency dielectric constant $\epsilon_m$ was determined from the calculated values of $\beta_{PF}$ for both amorphous and crystalline thin films. The high frequency dielectric constant value obtained from $J-E$ characteristics was compared to that calculated using the refractive index value, $\epsilon_m = n^2$, determined from ellipsometry studies to establish the dominant conduction mechanism in the present films. Ta$_2$O$_5$ thin films. The value of $\epsilon_m$ calculated from the slope of $\ln(J/E) = E^{-1/2}$ plot, $\epsilon_m = 4.48$, was in good agreement, for $\alpha = 2$, to that calculated using the refractive index value, $\epsilon_m = n^2 = 4.33$, for Ta$_2$O$_5$ thin film annealed at 750°C verifying Poole–Frenkel flow to be the dominant conduction mechanism in the present films. For crystalline thin films the high frequency dielectric $\epsilon_m$ constant obtained from $J-E$ characteristics was in good agreement, as shown in Table III, to that obtained from optical data for $\alpha = 2$. However, for amorphous thin films the value of parameter $\alpha$ was found to be less than 2 for a good agreement between $\epsilon_m$ values obtained from electrical and optical studies indicating that the trap concentration was lower in amorphous thin films as compared to crystalline thin films.

IV. CONCLUSIONS

Ta$_2$O$_5$ thin films exhibiting good structural, dielectric, and insulating properties were successfully deposited on Pt-coated Si, n+-Si, and poly-Si substrates by MOSD technique. The effects of postdeposition annealing temperature on the structural, optical, and electrical properties of amorphous and crystalline Ta$_2$O$_5$ thin films were investigated. The films were amorphous up to 600°C, and a crystalline orthorhombic phase with strong $\alpha$-axis orientation was obtained at 650°C. The surface morphology of the films was smooth with no cracks and defects while the grain size was found to increase with the increase in annealing temperature. The dielectric constant of amorphous thin films, annealed up to 600°C, was in the range 29.2–29.5 which matches well with the commonly reported value. However, crystalline thin films exhibited significantly enhanced dielectric constant in the range 45.6–51.7 for films annealed in the temperature range 650–750°C. The comparison of theoretical and experimentally calculated values of dielectric constant establish the orientation dependence of dielectric permittivity to be the main reason for the observed high dielectric constant in present Ta$_2$O$_5$ thin films. The loss factor did not show any appreciable dependence on the annealing temperature and was in the range 0.006–0.009 for films annealed in the temperature range 500–750°C. The films deposited on n+-Si and poly-Si substrates exhibited good film/silicon interfacial characteristics. The growth of the oxide layer at the interface was calculated to be lower than 2.5 nm at an annealing temperature of 750°C indicating that the combination of spin etching and MOSD technique was effective in minimizing the film-substrate interface reaction and providing good interfacial characteristics. The electrical properties of amorphous and crystalline Ta$_2$O$_5$ thin films were strongly influenced by the annealing temperature. The resistivity of amorphous thin films was found to increase with annealing temperature, while that of crystalline thin films was found to decrease. The decrease in leakage current of amorphous Ta$_2$O$_5$ thin films with increasing annealing temperature was attributed to the completeness of oxidation, and decrease in stress and defect density. The increase in leakage current density of crystalline thin films with annealing temperature was due to grain boundary contribution as the grain size was found to increase with annealing temperature and crystal induced defects as a result of stress arising due to phase transformation. Ta$_2$O$_5$ thin films exhibited high resistivity, measured at an applied electric field of 1 MV/cm, in the range $10^5$–$10^6$ Ω cm for amorphous and crystalline thin films. The $I-V$ characteristics were found to be ohmic at low fields and Poole–Frenkel effect was dominant at high fields. The value of the parameter $\alpha$ was found to increase with increase in annealing temperature indicating an increase in trap concentration with annealing temperature. The films exhibited good temperature and bias stability of dielectric properties.
The temperature coefficient of capacitance was in the range 52–114 ppm/°C for films annealed in the temperature range 500–750 °C. It was not possible to measure any appreciable change in the capacitance of amorphous films up to an applied electric field of 1 MV/cm indicating completeness of oxidation and low defect concentration. The bias stability of capacitance was 1.41% at an applied electric field of 1 MV/cm indicating completeness of oxidation and low defect concentration. The high resistivity, low temperature coefficient of capacitance was 1.41% at an applied electric field of 1 MV/cm indicating completeness of oxidation and low defect concentration. The bias stability of capacitance was 1.41% at an applied electric field of 1 MV/cm. The high dielectric constant, low dielectric loss, low leakage current density, and good temperature and bias stability suggest the suitability of Ta$_2$O$_5$ thin films as capacitor dielectric layer for DRAMS and integrated electronic applications.
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Tantalum oxide (Ta$_2$O$_5$) thin films were fabricated on Pt-coated Si, n+Si, and poly-Si substrates by metalorganic solution deposition technique. The effects of postdeposition annealing on the structural, electrical, and optical properties were analyzed. The Ta$_2$O$_5$ films were amorphous up to 600 °C. A well-crystallized orthorhombic phase with strong a-axis orientation was obtained at an annealing temperature of 650 °C. The refractive index was found to increase with annealing temperature and a value of 2.08 (at 630 nm) was obtained for films annealed at 750 °C. The electrical measurements were conducted on metal-insulator-metal (MIM) and metal-insulator-semiconductor capacitors. The dielectric constant of amorphous Ta$_2$O$_5$ thin films was in the range 29.2-29.5 up to 600 °C, while crystalline thin films, annealed in the temperature range 650-750 °C, exhibited enhanced dielectric constant in the range 45.6-51.7. The high dielectric constant in crystalline thin films was attributed to orientation dependence of the dielectric permittivity. The dielectric loss factor did not show any appreciable dependence on the annealing temperature and was in the range 0.006-0.009. The frequency dispersion of the dielectric properties was also analyzed. The films exhibited high resistivities of the order 10$^{12}$ - 10$^{15}$ Ω cm at an applied electric field of 1 MV/cm in the annealing temperature range of 500-750 °C. The measurement of current-voltage (I-V) characteristics in MIM capacitors indicated the conduction process to be bulk limited. The I-V characteristics were ohmic at low fields, and Poole-Frenkel effect dominated at high fields. The temperature coefficient of capacitance was in the range 52-114 ppm/°C for films annealed in the temperature range 500-750 °C. The bias stability of capacitance, measured at an applied electric field of 1 MV/cm, was better than 1.41% for Ta$_2$O$_5$ films annealed up to 750 °C. For a 0.15-μm-thick film, a unit area capacitance of 3.0 fF/μm$^2$ and a charge storage density of 22.3 fC/μm$^2$ were obtained at an applied electric field of 0.5 MV/cm.
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