Characterization of bias magnetron sputtered tantalum oxide films for capacitors

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Received 24 June 2008; revised 29 August 2008; accepted 24 October 2008

Tantalum oxide films have been deposited by sputtering of tantalum target in an oxygen partial pressure of $2 \times 10^{-4}$ mbar under various substrate bias voltages in the range from 0 to -150 V on glass and silicon substrates held at room temperature. The influence of substrate bias voltage on the chemical bonding configuration, crystallographic structure, electrical and dielectric properties has been systematically studied. The X-ray photoelectron spectroscopic studies reveal that the films are stoichiometric. The X-ray diffraction and Fourier transform infrared spectroscopic studies indicate that the films deposited under unbiased condition are amorphous in nature, whereas those formed at substrate bias voltages $\geq -75$ V are polycrystalline with orthorhombic $\beta$-phase. The electrical and dielectric properties of $\text{Ta}_2\text{O}_5$ films have been studied on the metal / insulator / metal (MIM) structure of Al/$\text{Ta}_2\text{O}_5$/Al. The dielectric constant of the films formed at unbiased condition has been found to be 15, while for those prepared at higher substrate bias voltage of -150 V has been found to be 23 due to the improvement in the crystallinity and packing density. The voltage - current measurements on the MIM structure indicate the decrease of leakage current density with the increase of substrate bias voltage.

Keywords: Tantalum oxide, Magnetron sputtering, Structure, Dielectric properties

1 Introduction

In recent years, high dielectric constant materials have been studied for the use in high density random access memory devices\(^1\). Among the available oxides, tantalum oxide ($\text{Ta}_2\text{O}_5$) received considerable attention because of its high dielectric constant, high refractive index and chemical and thermal stability with the promise of compatibility in the microelectronics processing. It also finds applications in antireflection coating on silicon solar cells and charge coupled devices\(^2\). The research work carried out on the tantalum oxide films was reviewed by Ezhilvalavan and Tseng\(^3\) for applications in ultra large scale integrated circuits and Chaneliere \textit{et al.} \(^4\) for advanced dielectric applications. Various thin film deposition techniques such as thermal oxidation of tantalum, electron beam evaporation, chemical vapour deposition, sol-gel, ion assisted deposition, pulsed laser deposition and dc/rf sputtering\(^5,6\) were employed for preparation of tantalum oxide films. Among these techniques, magnetron sputtering is the most industrially practiced technique for deposition of films on large area substrates. The advantage of biasing the substrate in magnetron sputtering leads to the generation of crystalline films at low substrate temperatures which enable to use the temperature sensitive substrates for device applications. The influence of oxygen partial pressure and substrate temperature on the structural, electrical and optical properties of tantalum oxide films was reported earlier\(^7\). In the present study, tantalum oxide films have been prepared by dc magnetron sputtering under various substrate bias voltages and their influence on the structural, electrical and dielectric properties have been studied.

2 Experimental Details

Thin films of tantalum oxide were deposited by employing dc reactive magnetron sputtering technique. The vacuum pumping system is capable of producing an ultimate pressure of $5 \times 10^{-6}$ mbar using the combination of diffusion and rotary pumps. Pure oxygen and argon were used as reactive and sputtering gases respectively. The required quantities of oxygen and argon gases were admitted into the sputter chamber through the fine controlled needle valves and their flow rates were monitored individually employing Tylan mass flow controllers. The $\text{Ta}_2\text{O}_5$ films were formed on p-type silicon (111) and glass substrates held at room temperature at a fixed oxygen partial pressure of $2 \times 10^{-4}$ mbar, sputtering pressure of $1 \times 10^{-3}$ mbar under various substrate bias voltages in the range 0 to -150 V. X-ray photoelectron spectroscopic (XPS) measurements
were carried out on the tantalum oxide films by employing Physical Electronics spectrometer (model PHI 5700) to determine the electron core level binding energies of the tantalum oxide films. The crystallographic structure of the films was analyzed by X-ray diffraction using X-ray diffractometer (Seifert model 3003 TT). The chemical binding configuration of the films formed on silicon substrates was obtained from the Fourier transform infrared spectrophotometer (Nicolet model 5700 FT-IR). The Ta$_2$O$_5$ thin film capacitors were formed with the configuration of Al/Ta$_2$O$_5$/Al by thermal evaporation of aluminum films as a bottom electrode on glass substrates followed by magnetron sputtered tantalum oxide film as dielectric and aluminum film as top electrode. The current-voltage characteristic of the capacitor was measured using Hewlett Peckard pA meter (model hp 4140B). The capacitance-voltage/frequency characteristics of the Ta$_2$O$_5$ capacitor were measured using LCR meter (Mioki model 3532-50) to determine the dielectric constant of the films.

3 Results and Discussion

Figure 1 shows a representative XPS survey scan of the Ta$_2$O$_5$ films formed at a substrate bias voltage of -150 V. The peak observed at about 284.6 eV was related surface with the carbon since they were exposed to the atmosphere before XPS study. The carbon contamination disappeared after 5 minutes of argon bombardment. The spectrum contained the characteristic peaks of tantalum oxide. The survey spectrum exhibited a peak at core level binding energy 26 eV related to the Ta 4f. The peaks were observed at 230 and 242 eV related to Ta 4d$_{5/2}$ and Ta 4d$_{3/2}$ respectively. The peaks observed at 403 and 467 eV related to the Ta 4p$_{3/2}$ and Ta 4p$_{1/2}$ respectively. Fig. 2a shows the narrow scan XPS spectra in the binding energy range of 25-30 eV. The core level binding energies of Ta 4f gives rise to two peaks at 26.4 and 28.2 eV respectively for Ta 4f$_{7/2}$ and Ta 4f$_{5/2}$ with spin orbit splitting of 1.8 eV, indicated the presence of tantalum in the oxidation state of Ta$^{5+}$. The core level binding energy of pure elemental Ta 4f$_{7/2}$ was 22 eV$^{10}$. The observed chemical shift in Ta 4f$_{7/2}$ was 4.4 eV which indicated that the films were stoichiometric in the phase of Ta$_2$O$_5$. Chong et al.$^{10}$ also obtained a chemical shift of 4.2 eV in rf sputtered Ta$_2$O$_5$ films. It is to be noted that the stoichiometric films exhibit the Ta 4f$_{7/2}$ peak at 26.3 eV$^{11}$. The core level binding energy of O 1s was 530.2 eV as shown in Fig. 2b. There was no significant variation in the binding energies in the films formed at different substrate bias voltages.
The X-ray diffraction spectra of the tantalum oxide films formed at different substrate bias voltages are shown in Fig. 3. The films formed under unbiased condition were amorphous in nature. As the substrate bias voltage increased to -75 V the films were transformed into polycrystalline phase due to the presence of diffraction peaks related to the (111), (261), (330) and (400) planes related to the orthorhombic β-phase of tantalum oxide. As the substrate bias voltage further increased to -150 V the intensity of the peaks increased which revealed the improvement in the crystallinity of the films. The observed diffraction peaks are in good agreement with the JCPDS data of tantalum oxide. The application of negative bias voltage to the substrate increases the energy of the positively charged particles bombarding the substrate and improved the process of sputtering on the surface of the growing films. The crystallinity of the films also increased with the bias voltage in rf reactive magnetron sputtered aluminum nitride films. The crystallite size of the films evaluated from the diffraction peak (400) increased from 12 to 20 nm with the increase of substrate bias voltage from 0 to -150 V respectively due to the improvement in the crystallinity of the films.

Figure 4 shows the Fourier transform infrared spectra of Ta$_2$O$_5$ films formed under various substrate bias voltages. The films formed at unbiased condition showed absorption band at about 630 cm$^{-1}$ and attributed to the O≡3Ta stretching mode of Ta$_2$O$_5$ in the amorphous phase. When the substrate bias voltage increased to -75 V, a shoulder like band was observed at 510 cm$^{-1}$ along with the diminished in the intensity of the band of 630 cm$^{-1}$. The presence of band at 510 cm$^{-1}$ was connected to the O≡3Ta stretching mode of Ta$_2$O$_5$ in the polycrystalline phase. With further increase of substrate bias voltage to -150 V, the intensity of the band at 510 cm$^{-1}$ was also increased along with the presence of a band at about 810 cm$^{-1}$ related to the Ta-O-Ta stretching mode. The appearance of absorption bands at 510 and 810 cm$^{-1}$ indicated the Ta$_2$O$_5$ films in polycrystalline phase. This observation revealed that the crystallinity of the films improved with the increase of the substrate bias voltage. In general, higher substrate temperatures (> 673 K) or post-deposition annealing of the films formed at room temperature is necessary to produce polycrystalline films of Ta$_2$O$_5$.

The frequency dependence of capacitance of tantalum oxide films formed at different substrate bias voltages are shown in Fig. 5. It is seen from the figure that the capacitance of the films decreased gradually with the increase of frequency. The capacitance of the films (at a fixed frequency of 1 MHz) increased from 9.0×10$^{-12}$ to 1.2×10$^{-11}$ F with the increase of substrate bias voltage from 0 to -150 V.

Figure 6 shows the variation of dielectric constant of tantalum oxide films formed at different substrate bias voltages. The dielectric constant of the films increased with the increase of substrate bias voltage. The dielectric constant of the films formed under unbiased condition was low value of 15 due to the amorphous nature as confirmed by XRD studies. The increase of dielectric constant to a value of 23 at a substrate bias voltage of -150 V was due to the improvement in the crystallinity of the films.
Figure 7 shows the dependence of leakage current density on the applied voltage of the tantalum oxide thin film capacitors. It indicated that the leakage current density decreased with the increase of substrate bias voltage at any fixed applied voltage. The high current density in the case of films formed under unbiased condition was due to the amorphous nature of the films. The low current density in highly biased films was because of polycrystalline nature of the films with the increase of packing density. At low electric fields, the current density increased almost linearly with the voltage which indicated that the films display nearly ohmic behaviour. Similar behaviour of variation in the leakage current density was also noticed in tantalum oxide capacitors formed on kapton substrates.

4 Conclusions

Tantalum oxide films were deposited on glass and crystalline silicon substrates held at room temperature by sputtering of tantalum target in an oxygen partial pressure of 2×10^{-4} mbar under various substrate bias voltages in the range 0 to -150 V by employing dc magnetron sputtering. The influence of substrate bias voltage on the chemical binding configuration, structural and electrical properties was systematically studied. X-ray diffraction studies confirmed that the films formed at unbiased condition were amorphous, while those deposited at substrate bias voltages ≥ -75 V were polycrystalline with orthorhombic β-phase of tantalum oxide. The presence of crystalline nature was also confirmed from the Fourier transform infrared spectroscopy. The dielectric constant of the films formed at unbiased condition was 15, whereas those deposited at a substrate bias voltage of -150 V showed a high value of 23 with low leakage current density due to the improvement in the crystallinity as well as the packing density. The high dielectric constant and low leakage current tantalum oxide films formed at the substrate bias voltage of -150 V are quite useful for thin film capacitors.

Acknowledgement

One of the authors (MCS) is thankful to the University Grants Commission for the award of Junior Research Fellowship under the “UGC Research Fellowships in Science for Meritorious students”. This work was carried out with the financial support of University Grants Commission, New Delhi through a sanctioned research project No. F. 30-4/2004 (SR).
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