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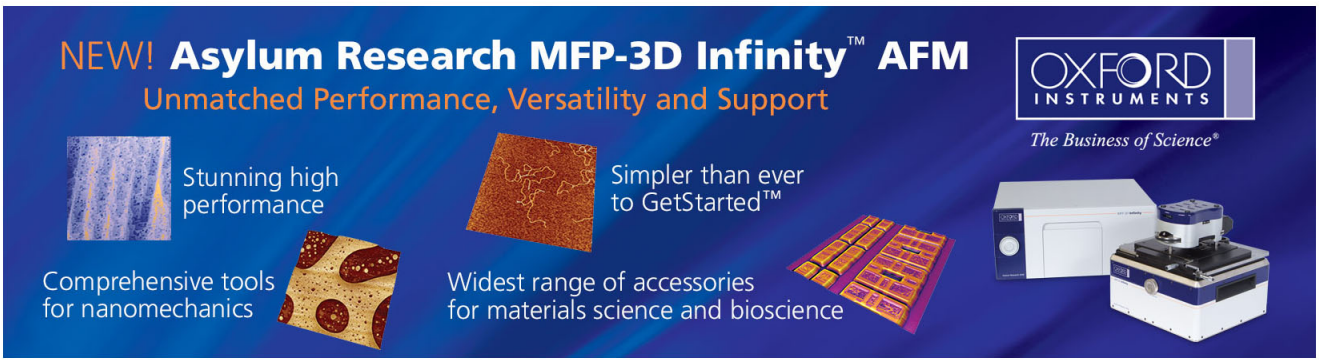

Electrical properties of Ta_2O_5 thin films deposited on Ta

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The electrical properties of reactively sputtered Ta_2O_5 thin films with Ta as the bottom electrodes were investigated. Ta films were deposited onto SiO_2/n-Si substrates by sputtering in Ar and *in situ* annealed at 700 °C for 10 min in N_2 at a chamber pressure of 20 mTorr. We compared the effectiveness of both as-deposited and annealed Ta bottom electrodes on the leakage characteristics of Ta_2O_5 thin films. We also envisaged the influence of the surface roughness and morphology of the Ta bottom electrode in modifying the resultant microstructure of the annealed Ta_2O_5 films. Present studies demonstrate the use of Ta as a potential bottom electrode material to replace the precious metal electrodes and to simplify the fabrication process of the Ta_2O_5 storage capacitor. © *1999 American Institute of Physics.* [S0003-6951(99)03317-3]

Tantalum pentoxide (Ta_2O_5) has been practically the most promising capacitor material to be used in the near future dynamic random access memories (DRAMs), because of its high dielectric constant, thermal and chemical stability, and good step coverage.[1,2] As the DRAM generation goes 256 M-bit and beyond, the DRAM fabrication process has become more and more complicated. This will cause the production cost of the high density DRAMs unacceptably high and will significantly degrade the device reliability. Thus, it is essential to develop a process technology that is simple and yet ensures high performance and high reliability.[3] Current semiconductor technology demands the use of low-resistivity metals as electrode materials for ultralarge scale integrated (ULSI) conduction lines and contact structures. In order for ULSI circuits manufacturing to minimize the cost of ownership aspect in the metallization process, several metallization technologies have been proposed. The evidential criteria in choosing the most probable are physical or material limitations (e.g., step coverage and resistivity) and manufacturing requirements such as process complexity, reliability, throughput, and total cost. Replacing the precious metals with a base metals like Al and Ni have been attempted in the mass production of multilayer ceramic chip capacitors.[4] More recently we have reported the electrical properties of Ta_2O_5 thin films deposited on Cu.[5] Al, Ni, and Cu electrodes are easily oxidized during deposition (sputtering) or in the annealing process. Consequently, annealing in low oxygen partial pressure (p-O_2) is indispensable and may cause the formation of oxygen vacancies in the ceramic bodies of the capacitors.

There have been several technical problems associated with the Ta_2O_5 films during the high temperature processing steps, necessary for their applicability to integrated circuits, which cause significant increase of the leakage current. This, obviously, limits their use in DRAMs in terms of the refresh characteristics of the cell. Another problem associated with Ta_2O_5 is the choice of bottom electrode. Usually poly-Si is used as the bottom electrode. However, since Si has stronger electron affinity than Ta, poly-Si cannot be used as the bottom electrode. The oxide materials deposited onto the Si (metal–oxide–semiconductor structure) cause interaction or atomic interdiffusion with Si at elevated temperatures which result in the formation of a lower dielectric constant interfacial layer of silicon oxide.[6] This problem becomes quite severe as the oxide thickness is reduced into the sub-micron range. The alternative is the use of a metal–semiconductor–metal (MIM) structure, i.e., to deposit the dielectric film on an intermediate base electrode which remain electrically conductive after exposure to an oxidizing environment at high temperatures. The bottom metal electrode layer also prevent the interdiffusion of silicon or oxygen across the interface, thus eliminating the formation of an undesirable interfacial layers. Ta metal can be adopted as the bottom electrode because it is thermodynamically and electrically compatible with Ta_2O_5 and it has excellent barrier property against diffusants.[7,8] Another advantage is the simplicity of the processing techniques, i.e., the dielectric film and the bottom electrode can be *in situ* made using the same target material and in a single sputtering machine followed by *in situ* annealing processing without being exposed to outside atmospheres, thereby avoids contamination if any, in between the processing steps. In this letter we report the preliminary experimental results of the effect of Ta as a bottom electrode material on the electrical and dielectric properties of reactively sputtered Ta_2O_5 thin films for the first time. The studies show the high reliability and quality of the Ta_2O_5 film for the possible integration into ULSI applications.

The n-type silicon wafer was cleaned by a standard cleaning process. The Ta bottom electrode on SiO_2/n-Si substrate with a thickness of 100 nm was deposited by direct current-magnetron sputtering from a high purity tantalum metal target (2.5 in. in diameter). The Ta film was prepared at a fixed power of 35 mW and at a constant pressure of 10 mTorr with Ar as the sputtering gas. The as-deposited Ta bottom layer was *in situ* annealed at 700 °C/10 min in N_2 at a chamber pressure of 20 mTorr. Ta_2O_5 films were deposited on to the $Ta/SiO_2/n$-Si bottom storage node electrode in the same sputtering machine without breaking the vacuum. The

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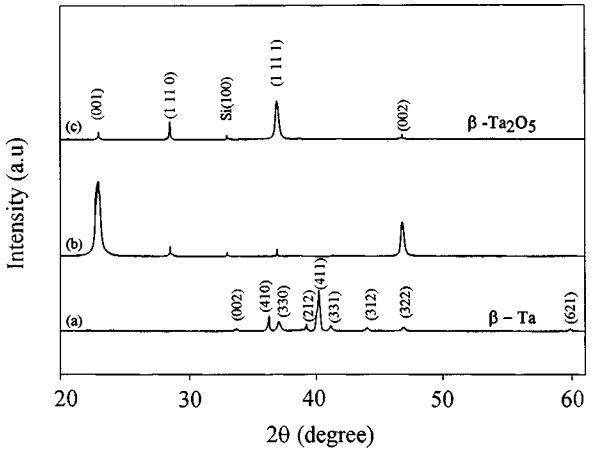

FIG. 1. XRD spectra of Ta and 30 s 800 °C O_2 RTA processed Ta_2O_5 films: (a) Ta film *in situ* annealed at 700 °C for 10 min in N_2, (b) Ta_2O_5 film sputtered on the as-deposited Ta, and (c) Ta_2O_5 deposited on the annealed Ta bottom electrodes.

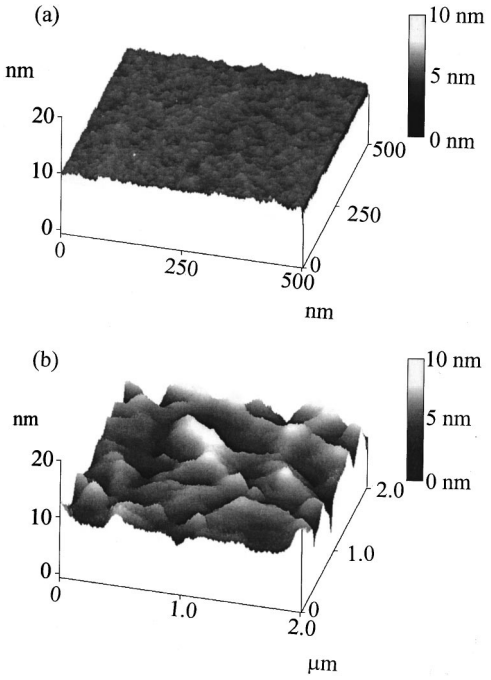

FIG. 2. AFM images of the RTA processed Ta_2O_5 film deposited on (a) as-deposited Ta and (b) annealed Ta bottom electrodes.

sputtering gas consists of 80% Ar and 20% O_2 mixture with a total pressure of 10 mTorr. More details on the deposition technique may be found in Refs. 5 and 6. Film thickness was estimated to be 100 nm by using a Tencor Alpha-step 200 profilometer. The rapid thermal annealing (RTA) of the Ta_2O_5 film was performed, before patterning the top electrode in a RTA furnace (Ulvac Sinku-Rico, HPC 700) at 800 °C for 30 s in O_2 ambient. The RTA process temperature (800 °C) and annealing time (30 s) were chosen based on our earlier study.[9] The heating rate used was the maximum heating rate of about 100 °C/s. The Pt top electrode with a thickness of 100 nm and diameters of 150, 250, and 350 μm were patterned by a shadow mask process. The current–voltage ($I-V$) characteristics of the Ta_2O_5 films were measured on the MIM structure with a delay time of 30 s using HP4145B semiconductor parameter analyzer. The capacitance–voltage ($C-V$) characteristic and the dielectric loss tangent were recorded at frequencies ranging from 100 Hz to 10 MHz with 0.5 V alternating current (ac) sweeping signal using HP4194A impedance-gain phase analyzer.

Four probe resistivity measurement and x-ray diffraction [(XRD), Model D5000, Siemens, Munich, FRG] were employed to identify the Ta and Ta_2O_5 phases of the sputtered films. The structure of the as-deposited Ta film on SiO_2/n-Si substrate is amorphous. However, Ta crystallizes after *in situ* annealing at 700 °C for 10 min in N_2 atmosphere inside the sputtering chamber, keeping the total pressure of about 20 mTorr. The resulting phase is identified as β-Ta (tetragonal) as shown in Fig. 1(a), with a resistivity of ~175 $\mu\Omega$ cm. Resistivity of the order of 30 $\mu\Omega$ cm or less were indicative of body-centered-cubic-Ta, while 160–200 $\mu\Omega$ cm was characteristic of β-Ta.[7,8,10] Detailed studies of XRD of Ta_2O_5 films deposited on as-deposited and *in situ* annealed Ta bottom electrode were carried out. The results showed that as-deposited Ta_2O_5 films were amorphous and the annealed Ta_2O_5 films crystallized into β-Ta_2O_5 (orthorhombic) irrespective of whether the bottom Ta electrode is amorphous or crystallized (β-Ta) [Fig. 1(b) and 1(c)]. In addition, it is to be noted that annealed Ta_2O_5 films exhibit a very strong preferred orientation i.e., peaks of certain reflections of the diffracting planes dominate the XRD pattern. The intensities of the (001) and (002) reflections dominate in the annealed Ta_2O_5 films deposited on the as-deposited amorphous Ta whereas (1 11 0) and (1 11 1) became predominant in the Ta_2O_5 films deposited on the annealed crystallized Ta bottom electrode. The earlier results demonstrate that the structure of the Ta bottom electrode and its surface morphology has significant influence on the crystallographic orientation of the deposited films. To elucidate this, the root-mean-square (rms) surface roughness and morphology of the as-deposited and annealed films were examined using atomic force microscopy [(AFM), Digital Instruments, Nano-Scope III]. The rms surface roughness of the as-deposited Ta bottom layer is ~0.315 nm, whereas the annealed Ta bottom electrode show a decreased rms value of ~0.249 nm. Compared to the annealed Ta_2O_5 film deposited on as-deposited Ta, the film sputtered on the annealed Ta electrode was having higher rms value i.e., the rms value increased from 0.277 to 1.394 nm (Fig. 2). The larger rms surface roughness of the annealed Ta_2O_5 films on the annealed Ta bottom electrode is probably due to the crystallization and grain growth of the bottom electrode itself.[11]

The important electrical characteristics of the dielectric material to be used as storage capacitors in DRAMs is the low leakage current density and reasonable high dielectric constant. Figure 3 shows the leakage current density versus electric field for the annealed Ta_2O_5 thin films deposited on the as-deposited Ta (a) and annealed Ta bottom electrode (b). Results in this study demonstrate that the Ta_2O_5 thin film deposited on the annealed Ta bottom electrode exhibit lower leakage current density of about 10^{-9} A/cm^2 at an applied field of 100 kV/cm. The difference in the leakage characteristics of the Ta_2O_5 film with respect to the as-deposited against the annealed Ta bottom electrode may be attributed to the effective reduction of oxygen vacancies through the grain boundaries of annealed Ta electrode. Although scan-

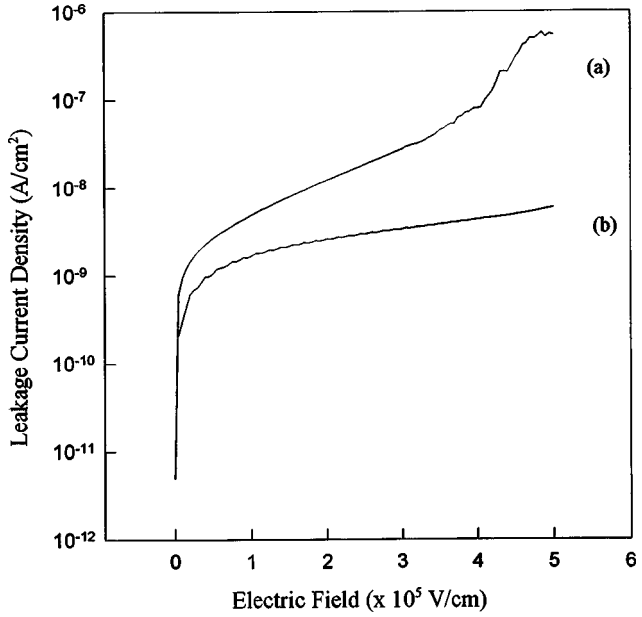

FIG. 3. Current–voltage characteristics of RTA processed Ta_2O_5 films deposited on (a) as-deposited Ta and (b) annealed Ta bottom electrodes.

ning electron microscope (Model S2500, Hitachi, Japan) observations indicate that both annealed Ta_2O_5 films deposited on the as-deposited and annealed Ta bottom electrodes exhibit smaller grain size distribution $\leqslant 1$ nm, larger grain boundary regions are distinctly visible in the case of Ta_2O_5 films deposited on annealed crystallized Ta bottom electrode. Root-mean-square surface roughness and morphology observations as shown in Fig. 2 also supports this results. These resultant grain and grain boundary modifications of the annealed Ta_2O_5 film may be resulted from the nature of surface conditions of the Ta bottom electrode on which the Ta_2O_5 film growth has taken place. That is, the crystallized Ta bottom electrode acts as an nucleation center for the large grain growth of the Ta_2O_5 films in comparison to the growth on the as-deposited Ta bottom layer. During RTA processing, the O_2 gas is decomposed into atomic oxygen (O*).[12] The atomic oxygen will be absorbed on the surface of the film and then diffused into the film, more easily through grain boundary defects. Since the atomic oxygen is a strong oxidizing agent, it is believed that O* will participate the reduction of defects of oxygen vacancies.

The dielectric constants of the Ta_2O_5 films were calculated from the accumulation capacitance at 100 kHz, the known area of the Pt electrodes of MIM capacitor and the ellipsometrically determined oxide thickness. The dielectric constants and the loss tangents of the Ta_2O_5 films deposited on the as-deposited and annealed Ta-bottom electrode are 35, 41, 0.02, and 0.03, respectively. Capacitance dispersion as a function of frequency from 100 Hz to 10 MHz were also studied to estimate the defect density contribution on the relaxation, and hence, its influence on the electrical properties. There are at least four possible defects namely, the interface defect, grain boundary defect, shallow trap levels, and oxygen vacancies, may often exist in the MIM capacitors lead to a dielectric relaxation as a function of frequencies. The grain boundary and the interface defect are considered to be a donor when it becomes neutral or positive by donating an electron. When an ac voltage is applied, the defect levels move up or down with respect to the conduction bands while the Fermi level remains fixed. A change of charge in the defect occurs when it crosses the Fermi level. Therefore, the defect density calculations can be done from the measurement of the real capacitance (C) and the imaginary part of the capacitance (C^*) as a function of frequency. Once C^* is known, the defect density can be obtained from the relation $D_{\mathrm{df}}=C^*/qA$, where A is the metal plate area and q is the elemental charge.[13] The defect density of Ta_2O_5 thin films deposited on annealed Ta bottom electrode is $7.37 \times 10^{10}\,\mathrm{cm}^{-2}\,\mathrm{V}^{-1}$, which is two orders smaller than that is observed in perovskite based dielectric films such as $Ba_{(1-x)}Sr_xTiO_3$ which exhibit significant dielectric relaxation at higher frequencies.[14] From the capacitance dispersion studies, we envisage that the dielectric relaxation of Ta_2O_5 films on Ta is less pronounced and it has least contribution from the defects, yet preserving lower leakage current density.

Time-dependent dielectric breakdown (TDDB) is a characteristic of the intrinsic materials, the method of processing, and electrode materials. TDDB studies demonstrate that Ta_2O_5 MIM films with Ta as the bottom electrode can also survive the 10 years life time at a stress field of $\geqslant$700 kV/cm. We have therefore, successfully demonstrated the effective use of Ta as a possible bottom electrode material replacing the conventional precious metal electrodes for Ta_2O_5 film storage capacitors. Usage of Ta as an electrode will significantly reduce process complexity and the production cost of future high density DRAMs.

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