Communications

Metal–Organic CVD of Tantalum Oxide from *tert*-Butylimidotris(diethylamido)tantalum and Oxygen**

By *Hsin-Tien Chiu,* Chun-Nan Wang*, and *Shiow-Huey Chuang*

Tantalum oxide is a high-dielectric material under intensive investigation for current and future generation dynamic random access memories (DRAMs).[1] In most cases, tantalum alkoxide complexes (such as $Ta(OEt)_5$) coupled with oxygen gas are employed as the precursors in the growth of tantalum oxide thin films by CVD.[2–5] To obtain device-quality tantalum oxide, the as-deposited films are often thermally treated in an oxidation environment. One drawback of using tantalum alkoxides is that, due to their low volatility, a high vaporization temperature is usually required. The reason for the low volatility is that these tantalum alkoxides frequently exist as high molecular weight dimers, $[Ta(OR)_5]_2$.[6] Clearly, replacing these alkoxides with more volatile monomeric Ta precursors could greatly improve the process. A monomeric complex $({}^tBuN)Ta(NEt_2)_3$,[7] *tert*-butylimidotris(diethylamido)tantalum (TBTDET), has been successfully used to grow tantalum nitride thin films by CVD.[8] At room temperature, TBTDET is a liquid with reasonable volatility. It is very likely that, under oxidizing conditions, it can be employed to grow high-quality tantalum oxide thin films. Here we report the results of our preliminary exploration. A similar strategy, using $Ta(NMe_2)_5$ to grow tantalum oxide thin films, has recently been reported.[9]

An atomic force microscopy (AFM) image of a sample, deposited at 873 K, is shown in Figure 1a. The root mean square roughness of the surface was estimated to be 2.3 nm. Cross-sectional scanning electron microscopy (SEM) images indicated that the films had columnar structures. From these images, the film thickness was measured and growth rates were estimated to be 0.6–2 nm min^{-1}. Raising the precursor vaporization temperature and optimizing other deposition parameters could increase the growth rate. A thin layer (several nanometers) of SiO_2 probably exists between the as-deposited thin film and the substrate.[4,10] The films were essentially amorphous, as indicated by X-ray diffraction (XRD). X-ray photoelectron spectroscopy (XPS) showed that tantalum and oxygen were the major components on the surface of the films. The binding energy of the O_{1s} electron was 532.0 eV, while the binding energies of $Ta_{4f_{7/2}}$ and $Ta_{4f_{5/2}}$ signals were 26.7 eV and 28.6 eV, respectively, for several samples. This result agrees with the literature data for tantalum oxide.[11] Some adventitious carbon was also found, showing a minor C_{1s} signal near 284.5 eV. Sputtering the surface with Ar^+ ions decreased the signal intensity to the XPS detection limit. During sputtering, preferential removal of oxygen was observed, leaving some Ta atoms in the metallic state, which is consistent with previously reported findings.[12] The N_{1s} signal is below the XPS detection limit, indicating that the

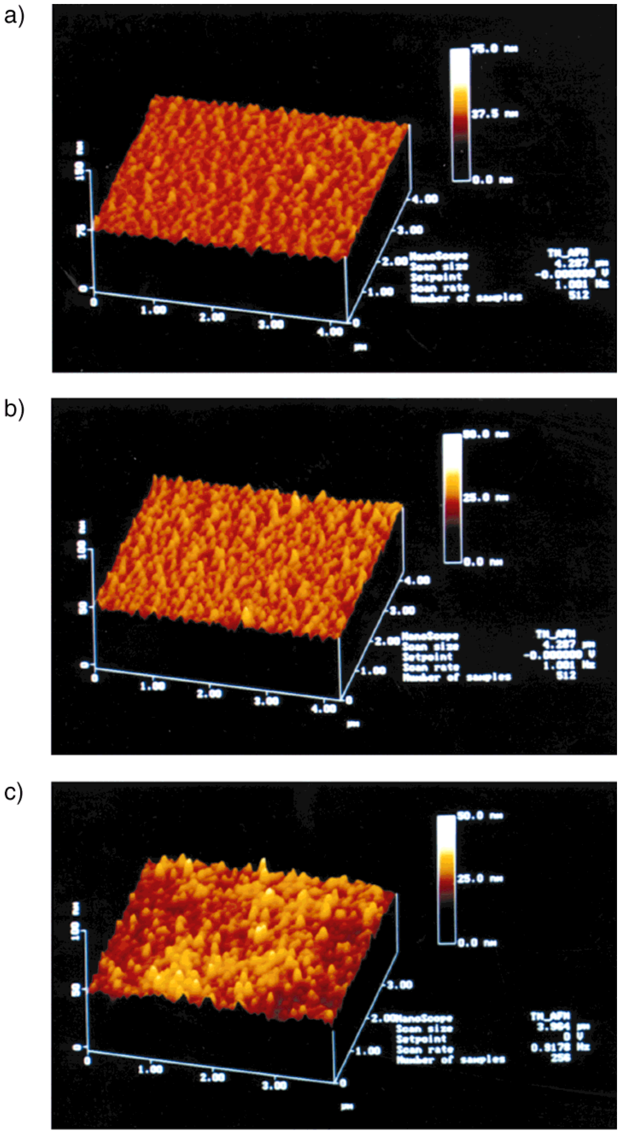

Fig. 1. AFM images of tantalum oxide thin films grown at 873 K. a) As-deposited under O_2. b) Deposited under O_2 followed by annealing at 1123 K under O_2 (1 atm) for 2 h. c) As-deposited in the presence of H_2O vapor followed by annealing at 1123 K under O_2 (1 atm) for 2 h.

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concentration of N in the films is low (below 2 %). Auger depth profile studies showed uniform Ta and O distributions within the films. Using nuclear magnetic resonance (NMR) spectroscopy, and mass spectroscopy (MS), $Me_2C=CH_2$, $CH_3C\equiv N$, Et_2NH, Et_2NOH, and NO were positively identified as the major volatile by-products.

For device applications, heat treatment under an oxygen atmosphere is considered to be an important step in obtaining high-quality tantalum oxide thin films from tantalum alkoxides.[2–5] This process was applied to the films prepared in this study. For example, a sample grown at 873 K was annealed at 1173 K under 1 atm of O_2 for 2 h. After this process, the surface roughness increased from 2.3 nm to 4.2 nm, as shown by AFM, Figure 1b. The film thickness shrank slightly, to about 95 % of its original value, while XRD indicated that the crystallinity of the film had increased. The XRD also showed characteristic reflections of the β-Ta_2O_5 phase. It is known that SiO_2 layers between tantalum oxide films and Si substrates thicken after heat treatment under oxygen,[4,10] and we believe that this phenomenon occurred in our study. We also explored the possibility of growing tantalum oxide thin films from TBTDET and H_2O (vaporized at 273 K). These films showed higher roughness than the films deposited under O_2. This probably resulted from a gas phase reaction between TBTDET and H_2O, a clear disadvantage. Other analyses (XRD, XPS, and Auger) indicated that the films were amorphous tantalum oxide. They also crystallized into the β-Ta_2O_5 phase after thermal treatment under 1 atm of O_2 at 1173 K. The roughness barely changed. The sample in Figure 1c showed a value of 8.4 nm after the treatment.

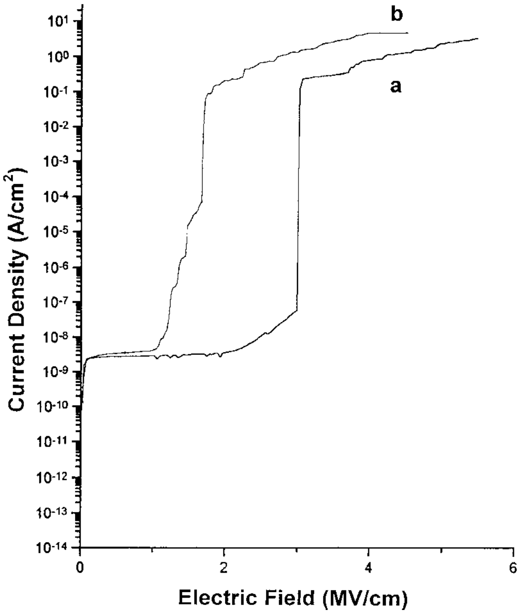

Fig. 2. Leakage current density versus applied electric field of tantalum oxide thin films deposited at 873 K followed by annealing at 1123 K under O_2 (1 atm) for a) 30 min, b) 1 h.

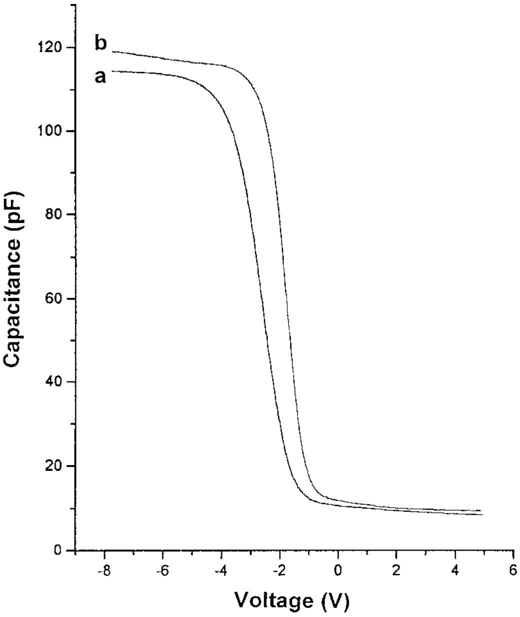

Fig. 3. C–V curve of tantalum oxide films deposited at 873 K followed by annealing at 1123 K under O_2 (1 atm) for a) 30 min. b) 1 h.

Metal oxide semiconductor (MOS) capacitors with an Al/Ta_2O_5/p-Si/Al structure were fabricated from the tantalum oxide thin films grown from TBTDET to evaluate the potential usefulness of this process. A layer of tantalum oxide (180 nm) was grown on p-Si(100), employing the process, and using O_2 as the carrier gas. The deposition temperature was 873 K, while the annealing process was carried out at 1123 K under an O_2 atmosphere. Al electrodes were grown above the tantalum oxide layer (Al thickness 500 nm), and below the silicon substrate (Al thickness 300 nm), using e-beam evaporation. The final top Al electrodes were processed into squares of 300 × 300 μm^2. Without thermal annealing, the device showed a high leakage current of 2×10^{-4} A cm^{-2}, at an electric field strength of 0.5 MV cm^{-1}, while the breakdown voltage was 0.7 MV cm^{-1}. For samples annealed for 30 min, the I–V and C–V curves are shown in Figures 2 and 3, respectively. The leakage current is below 1×10^{-8} A cm^{-2} for a field of 2 MV cm^{-1}, while the breakdown voltage is 3 MV cm^{-1}. From the C–V curve obtained at 1 MHz, the dielectric constant is estimated to be about 22. This number represents the combined dielectric properties of the Ta_2O_5 and the thin SiO_2 layer underneath it. When the annealing time was 1 h, the leakage current was below 1×10^{-8} A cm^{-2} for an electric field of 1 MV cm^{-1}, while the breakdown voltage dropped to 1.6 MV cm^{-1} (Fig. 2). The decrease in the breakdown voltage is attributed to an increase in the surface roughness of the tantalum oxide film. From Figure 3, the dielectric constant is estimated to be a higher value, 35. These data are comparable to the values reported for tantalum oxide thin films prepared using various techniques.[2–5,10,13–19]

In this preliminary report, we have demonstrated that TBTDET, a monomeric tantalum-containing molecule with a vapor pressure higher than that of $Ta(OEt)_5$, and other tantalum alkoxides, can be used as a precursor to grow tantalum oxide thin films by CVD for device application. Using this precursor, a Ta_2O_5 film with a thickness of 180 nm had a leakage current density below 1×10^{-8} A cm^{-2} for an electric field strength of 2 MV cm^{-1}, and a breakdown voltage of 3 MV cm^{-1}. The dielectric constant was 22. Further optimization of the process could lead to tantalum oxide thin films with better electric properties. Investigation is in progress.

Experimental

The CVD experiment was carried out in a cold-wall low-pressure reactor with a base pressure of 1×10^{-5} torr. TBTDET was vaporized at 313 K using Ar flowing at 10 sccm as the carrier gas. The deposition of thin films on p-Si(100) was carried out at temperatures between 573 K and 873 K. With oxygen flowing at 200 sccm, the pressure during the deposition was maintained at 1 torr.

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Synthesis of New Liquid Mixed Sr–Ta and Sr–Nb Alkoxides as CVD Precursors for Metal Oxide Thin Films

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Thin films of $SrBi_2Ta_2O_9$ (SBT) have been investigated for possible application in ferroelectric memories. The film was previously prepared from $Sr[Ta(OC_2H_5)_6]_2$, **1**, and $Bi(CH_3)_3$ by metal–organic chemical vapor deposition (MOCVD).[1] The Sr/Ta and Bi/Ta ratios in the film were easily controlled by the use of **1**. Since, above 170 °C, **1** dissociates to a non-volatile polymer $[Sr(OC_2H_5)_2]_\infty$ and a volatile dimer $[Ta(OC_2H_5)_5]_2$, the vapor composition of the bubbling feed is rich in Ta. To keep the Sr/Ta ratio of the vapor stoichiometric, we made a new precursor by adding 0.4 mol $Sr(OC_2H_5)_2$ to 1 mol of **1**.[2] However, this precursor is solid at room temperature, and its composition changes during use. In the present study, we have developed a new precursor $Sr[Ta(OC_2H_5)_5(OC_2H_4OCH_3)]_2$, **2**, which is liquid at room temperature and does not dissociate at 190 °C. We have investigated the deposition behavior of **2**.

Recently, CVD of strontium tantalate thin films was carried out using the thermally stable, novel precursor, $Sr\{Ta[OEt]_5[OCH_2CH_2N(CH_3)_2]\}_2$, which is liquid at room temperature.[3] A patent claims novel precursors, $Sr\{Ta[OR^1]_{6-x}[ORX(R^2)(R^3)]_x\}_2$, X = N or O, and discloses two examples for X = N, but no example for X = O.[4]

The new precursor, **2**, has been created from the reaction of $Ta(OC_2H_5)_5$ with $Sr(OC_2H_4OCH_3)_2$, and purified by distillation. Its molecular weight, measured by the benzene cryoscopic method, is 1050 (calcd. for monomer **2**: 1050.3), so its complexity is 1.0. Its melting point is below 0 °C. It is completely miscible with toluene, THF, hexane, and butyl acetate.

The compound was characterized by chemical analysis, mass spectroscopy, ^1H nuclear magnetic resonance (NMR) spectroscopy, and Fourier transform infrared (FTIR) spectroscopy. Electron impact mass spectroscopy (EI-MS) (Fig. 1) shows that four kinds of species come from their parent molecules:

$$\begin{aligned}&SrTa_2(OEt)_9(OC_2H_4OCH_3)_3(1080) \xrightarrow{-OEt}\\ &\quad SrTa_2(OEt)_8(OC_2H_4OCH_3)_3^+(1035) \xrightarrow{-Ta(OEt)_5}\\ &\qquad SrTa(OEt)_3(OCH_2CH_2OCH_3)_3^+(629) \qquad (1)\end{aligned}$$

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