行政院國家科學委員會專題研究計畫成果報告

分子化合物合成無機材料之新方法(二)
NEW MOLECULAR ROUTES TO INORGANIC MATERIALS (2)

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一、中文摘要

本計畫繼續本研究室之研究，以分子化合物為前驅物，合成無機材料. 研究發現以$(Bu^tN)Ta(NEt_2)_3$ 為前驅物，可以經化學氣相沉積成長 Ta_2O_5 薄膜.

關鍵詞：五氧化二鉭、化學氣相沉積、薄膜

I. Abstract

Using tertbutylimidotris(diethylamido)-tantalum (TBTDET) and oxygen, amorphous tantalum oxide thin films, characterized by x-ray photoelectron spectroscopy (XPS), were grown by chemical vapor deposition (CVD) at 150 Pa between 573 and 873 K. After annealed at 1123 K under oxygen (1 atm), the films crystallized into β-Ta_2O_5, as indicated by x-ray diffraction (XRD). Metal oxide capacitors with a Al/Ta_2O_5/p-Si/Al structure were fabricated. For a Ta_2O_5 film with a thickness of 180 nm, the leakage current density was below 1×10^{-8} A/cm^2 at an electric field strength of 2 MV/cm and the breakdown voltage was 3 MV/cm. The dielectric constant was 22.

Keywords: Ta_2O_5, Chemical Vapor Deposition, Thin Film

II. Introduction

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 were employed as the precursors to grow tantalum oxide thin films by chemical vapor deposition (CVD).[2-5] To obtain device quality tantalum oxide, the as-deposited films were often thermally-treated under an oxidation environment. One draw-back of using tantalum alkoxides is that due to their low volatility, high vaporization temperature is frequently required. The origin of 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 improve the process greatly. Previously, a monomeric complex $(Bu^tN)Ta(NEt_2)_3$,[7] tertbutylimido-tris(diethylamido)tantalum (TBTDET), has been utilized to grow tantalum nitride thin films by CVD successfully.[8] TBTDET is a liquid at room temperature with reasonable volatility. It is very likely that under an oxidizing condition, it can be employed to grow high quality tantalum oxide thin films. Here we report our preliminary exploration results. A similar strategy has been reported recently using $Ta(NMe_2)_5$ to grow tantalum oxide thin films.[9]

III. Results and Discussion

The CVD experiment was carried out in a cold-wall low-pressure reactor with a base pressure of 1 x 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 and 873 K. With oxygen flowing at 200 sccm, the pressure during the deposition was maintained at 1 torr. An atomic force micrograph (AFM) 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 micrographs (SEM) indicated that the films had columnar structures. From these images, growth rates were estimated to be 0.6 - 2 nm/min. The growth rate could be increased by raising the precursor vaporization temperature and optimizing other deposition parameters. A thin layer of SiO_2 of several nanometers probably existed between the as-deposited thin film and the substrate.[4,10] The films were essentially amorphous as indicated by X-ray diffraction (XRD) studies. X-ray photoelectron spectroscopy (XPS) showed that tantalum and oxygen were the major components on the surface of the films. The binding energy of O_{1s} electron was observed at 532.0 eV while the binding energies of $Ta_{4f7/2}$ and $Ta_{4f5/2}$ signals were observed at 26.7 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 minor C_{1s} signal near 284.5 eV. Sputtering the surface with Ar^+ ions decreased the signal intensity to the detection limit of XPS. Preferential removal of oxygen during sputtering was observed, leaving some Ta atoms in the metallic state. This observation is consistent with a literature report.[12] For most of the samples, it was difficult to detect N_{1s} signal, probably due to a low concentration of nitrogen in the films. Unless nitrogen exists in concentration high enough, its signal would be overwhelmed by a $Ta_{3p3/2}$ signal nearby. 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 byproducts.

According to literature, heat treatment under oxygen atmosphere is an important step to obtain high quality tantalum oxide thin films from tantalum alkoxides for device applications.[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 1atm of O_2 for 2 h. After this process, the roughness of the surface increased from 2.3 nm to 4.2 nm as shown by an AFM image in Figure 1b. The film thickness shrank slightly to about 95% of its original value. The crystallinity of the film also increased as suggested by XRD. It showed characteristic reflections of β-Ta_2O_5 phase. It is known from reports in literature that SiO_2 layers between tantalum oxide films and Si substrates thickened after heat treatment under oxygen.[4,10] We believe that this phenomenon occurred in our study too. We also explored the possibility to grow tantalum oxide thin films from TBTDET and H_2O (vaporized at 273 K). The films showed higher roughness than the films deposited under O_2. An example, which had a roughness of 8.5 nm. 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 crystallized into β-Ta_2O_5 phase after thermally treated

under 1 atm of O_2 at 1173 K too. The roughness barely changed. For the sample shown in Figure 1c, it showed a value of 8.4 nm after the treatment.

Metal-oxide-semiconductor (MOS) capacitors with a 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) using the process mentioned above. The deposition temperature was 873 K while the annealing process was carried out at 1123 K when needed. 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 x 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 while the breakdown voltage was at 0.7 MV/cm. 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 at a field of 2 MV/cm while the breakdown voltage is at 3 MV/cm. From the C-V curve obtained at 1 MHz, the dielectric constant is estimated to be about 22, taking the SiO_2 layer between the Ta_2O_5 layer and the Si substrate into consideration. When the annealing time was 1 h, the leakage current was below 1×10^{-8} A/cm^2 at an electric field of 1 MV/cm while the breakdown voltage dropped to 1.6 MV/cm (Figure 2). The decrease in the breakdown voltage is attributed to an increase in the surface roughness of the tantalum oxide film. The dielectric constant is estimated from Figure 3 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]

IV. Conclusion

In this preliminary report, we have demonstrated that tertbutylimido-tris(diethylamido)tantalum (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 at an electric field strength of 2 MV/cm and a breakdown voltage 3 MV/cm. The dielectric constant was 22. Further optimization of the process could grow tantalum oxide thin films with better electric properties. Investigation is in progress.

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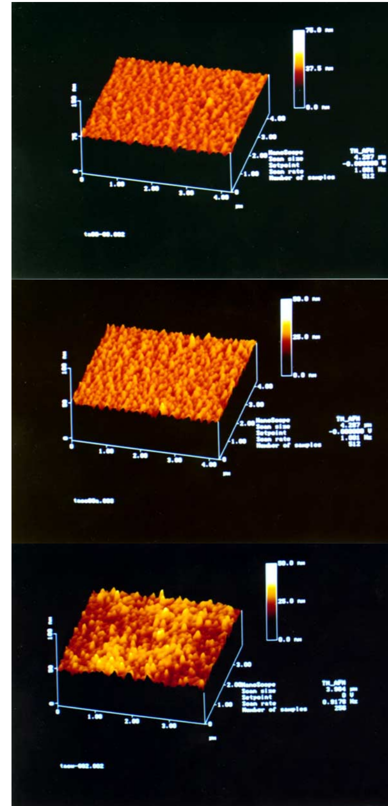

FIG. 1. Atomic force micrographs of tantalum oxide thin films grown at 873 K. (a) As-deposited under O_2, (b) deposited under O_2 followed by annealing at 1123 K under O_2 (1 atm) for 2 h, and (c) as-deposited in the presence of H_2O vapor.

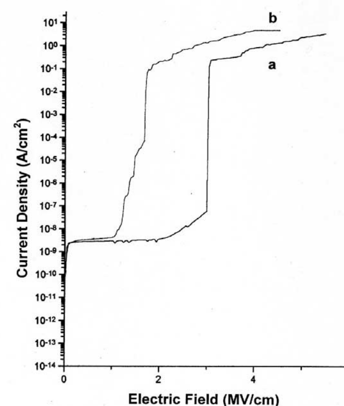

FIG. 2. Leakage current density versus applied electric field of tantalum oxide thin films deposited at 873 K followed by annealing at 1123 K under O_2 (1atm) for (a) 30 min and (b) 1 h.

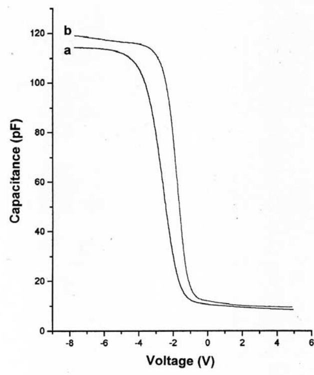

FIG. 3. C-V curve of tantalum oxide films deposited at 873 K followed by annealing at 1123 K under O_2 (1atm) for (a) 30 min and (b) 1 h.