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Highly conformal atomic layer deposition of tantalum oxide using alkylamide precursors

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Abstract

Atomic layer deposition of highly conformal films of tantalum oxide were studied using tantalum alkylamide precursors and water as the oxygen source. These films also exhibited a very high degree of conformality: 100% step coverage on vias with aspect ratios greater than 35. As deposited, the films were free of detectable impurities with the expected (2.5–1) oxygen to metal ratio and were smooth and amorphous. The films were completely uniform in thickness and composition over the length of the reactor used for depositions. Films were deposited at substrate temperatures from 50 to 350 °C from precursors that were vaporized at temperatures from 50 to 120 °C. As deposited, the films showed a dielectric constant of 28 and breakdown field consistently greater than 4.5 MV/cm.

Keywords: Tantalum oxide; Atomic layer deposition; Precursors

1. Introduction

Tantalum(V) oxide (Ta_2O_5) has been used extensively as an insulating layer in discrete capacitors and shows a high potential for semiconductor applications [1] such as an insulating dielectric in the capacitive element in memory devices such as dynamic random access memory (DRAM) [2]. Future DRAM designs may use capacitors made from long narrow holes with high aspect ratios in place of conventional flat surface capacitors [3]. Atomic layer deposition (ALD) is an ideal method for depositing highly conformal films and it offers the additional benefit of smooth films, precise thickness control and precise composition control [4]. Tantalum(V) oxide has been prepared using the ALD method from several sources. Using water as an oxygen source, the ethoxide precursor [5] ($Ta(OCH_2CH_3)_5$), the chloride precursor [6] ($TaCl_5$) and the iodide precursor [7] (TaI_5) have all been used to produce ALD films over a modest temperature range (100–400 °C). The ethoxide precursor and the chloride precursor have also been used together without water to produce tantalum oxide films under ALD conditions in a temperature range of 275–400 °C [8]. Here we report the ALD of tantalum(V) oxide using two amide precursors and water as an oxygen source. Due to their higher reactivity with a hydroxylated surface, the films produced from these precursors show unprecedented step coverage.

2. Experimental

ALD was performed in a flow reactor (Fig. 1). The reactor was a stainless steel tube (76 cm in length and 3.7 cm in diameter) heated in a tube furnace. Precursors and nitrogen gas were introduced into the reactor through a bored out flange at one end of the tube. Tetrakis(dimethylamido)tantalum(V) ($Ta(NMe_2)_5$) was obtained from Strem Chemical Company and tris(diethylamido)(ethylimido)tantalum(V) ($Ta(NEt)(NEt_2)_3$) was obtained from Aldrich Chemical Company. All substrates were exposed to a UV lamp (in air to generate ozone) for 3 min (sufficient to restore the hydrophilic character of a HF dipped silicon wafer)

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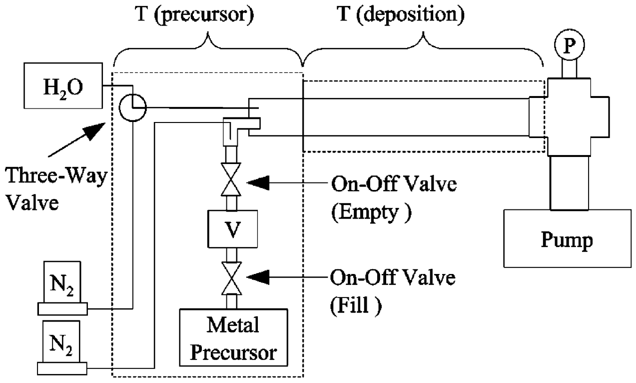

Fig. 1. Schematic diagram of the deposition system.

immediately prior to deposition. Silicon (1 0 0) substrates were cleaned in a 48% HF solution for 5 s prior to UV/ozone treatment. Glassy carbon substrates (Alfa), for RBS, were mechanically polished with diamond powder. Quartz substrates (Gem Dugout), for XRD analysis, were cut 6° from (0 0 0 1) to ensure a low background. Patterned silicon substrates (Infineon) were used for step coverage measurements. Nitrogen flow in the reactor was maintained at 0.020 standard l/min and the pressure in the chamber was maintained at 0.10 Torr. Thus, the linear velocity of the gas flow in the deposition chamber was approximately 20 m/s. The ALD reaction cycle consisted of a single tantalum dose, followed by a nitrogen purge (typically 5 s), then a water dose, followed by another nitrogen purge (typically 5 s).

Water vapor was introduced into the reactor by a three-way gas-chromatography (GC) valve connected to the reactor by a stainless steel feed-through (0.04 cm inner diameter). The GC valve was positioned electronically in two states to allow either nitrogen gas (purge state) or water vapor (dose state) to flow into the reactor. A single water dose consisted of positioning the GC valve in the dose state for 1 s, during which time 1 μM of water vapor flowed into the deposition chamber. Then the valve was returned to its purge state.

Heating each tantalum precursor to 120 °C was found to produce a vapor pressure of at least 1 Torr. $Ta(NEt)(NEt_2)_3$ has a reported vapor pressure of 0.10 Torr [9] at 95 °C and $Ta(NMe_2)_5$ has a reported vapor pressure of 0.6 Torr at 106 °C [10]. To deliver tantalum precursor vapor, the bottom on–off valve was opened for 1 s to fill the volume V (35 ml) with tantalum vapor at its equilibrium vapor pressure. After the bottom on–off valve was closed, the on–off valve on top of volume V was then immediately opened for 1 s to allow the tantalum precursor to enter the deposition chamber.

3. Film characterization

The film composition and area density were determined from by RBS (General Ionics Model 4117 spectrometer). Thickness and refractive index were determined by a Rudolph Research AutoEl-II ellipsometer at a wavelength of 632.8 nm. The film thickness and density were also determined using XRR and the crystallinity of the films were determined by XRD both using a Scintag XDS 2000 instrument with Cu Kα radiation (0.154 nm wavelength). Cross-sectional images were obtained with SEM (FEI Strata DB235). The film surface morphology was analyzed with a Digital Instruments Nanoscope VI atomic force microscope (AFM) with a silicon tip in the tapping mode. In situ mass measurements were made using an Inficon Technologies bakeable quartz crystal microbalance (QCM). Films prepared for electrical characterization were deposited on platinum-coated silicon substrates. After film deposition Pt contacts (50-nm thick) were evaporated onto the film using an Edwards e-beam evaporator, thus forming parallel plate capacitors with an area of 1.0×10^{-3} cm^2 and a top and bottom electrode made of platinum. Current–voltage measurements were made using a Keithley 2400 source meter and capacitance measurements were performed using a 4275a-001 HP LCR meter.

4. Results

The reaction between water vapor and each metal precursor was found to be highly efficient. An exact saturating dose of the precursor resulted in film deposition on every surface in the deposition zone with no film, powder, or residual precursors detected on any of the surfaces after the deposition zone. Additional precursor beyond a saturating dose did not increase the film growth while an under-saturating dose resulted in uneven deposition of film thinner than expected. Each dose consumed 0.19 ± 0.03 μM of precursor, which was the dose that would have been required to produce films with the observed area densities (0.2 nM Ta/cm^2 from both XRR and RBS) on every surface in the deposition zone (944 cm^2).

Under ALD conditions, the deposition rate from both precursors was 0.065 ± 0.002 nm per cycle. No nucleation delay was observed on any of the substrates used. As determined optically (ellipsometry and by visual diffraction), film thickness was highly uniform ($<1\%$ variation) along the length (46 cm) of the heated deposition zone. The growth rate was constant (independent of the number of cycles) from 10 cycles to 1000 cycles. The refractive index for the as-deposited films was 2.1 ± 0.02. RBS analysis showed the expected 1:2.5 metal to oxygen ratio and an area density per ALD cycle of 1.2 ± 0.05 metal atoms/nm^2 (Fig. 2). Carbon and nitrogen were not detected in the films ($<$ 0.25 at.%). XRR analysis was used to measure film thickness and determine the film density for each metal oxide. The films were determined to have a bulk density

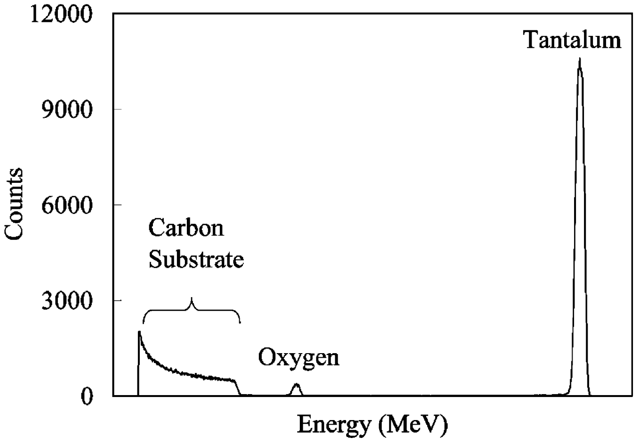

Fig. 2. RBS data for a tantalum oxide film grown at 250 °C.

of 6.6 g/cm^3 (80% of the density of crystalline tantalum oxide). The ratio of area density (measured by RBS) and the film thickness (from ellipsometry) verified the bulk density of the film measured using XRR. AFM analysis films showed an RMS roughness that was less than 1% of the film thickness and XRD analysis showed the films to be amorphous as deposited independent of thickness. For both precursors, ALD conditions could be extended to temperatures as low as 50 °C with sufficient delay (300 s) between doses to allow for removal of unreacted precursor. The upper limit to ALD was determined by the thermal stability of each precursor. The tetrakis(dimethylamido)tantalum(V) ($Ta(NMe_2)_5$) could be used in a controlled fashion up to 250 °C while the tris(diethylamido)(ethylimido)tantalum(V) ($Ta(NEt)(NEt_2)_3$) could be used up to 350 °C. At temperatures higher than these compositional and thickness control was lost. With sufficient purging between precursor introduction, the bulk properties of the film were not found to vary significantly in the temperature range from 50 to 350 °C.

The step coverage was determined to be 100% in a patterned wafer with elliptical vias $0.17\times0.30\times7.3$ μm^3 deep etched in silicon (Fig. 3). The exposure of each precursor on a flat substrate was approximately 100 L, while for these high aspect ratio structures approximately 30 000 L was used to ensure complete coverage. This high exposure was achieved by increasing the dose (more moles of precursor entering the reactor), increasing the time spent in the reactor (lowering the gas flow rate), or a combination of the two. These high exposures were not found to affect other film properties.

In situ film deposition was studied in real time using a QCM. A mass increase after introduction of the metal precursor was observed within the sampling time of the QCM (0.2 s) indicative of a fast reaction between the metal amide and the surface (assumed to be hydroxylated) (Fig. 4). Additional metal doses (beyond a saturating dose) did not produce a further mass increase, demonstrating that the reaction of the metal precursor was self-limiting. A mass decrease was observed immediately after the introduction of water. The water-associated mass decrease also occurred faster than the time resolution of the QCM. A proposed mechanism consistent with the QCM observations involves two simple half reactions. First the metal amide precursor,

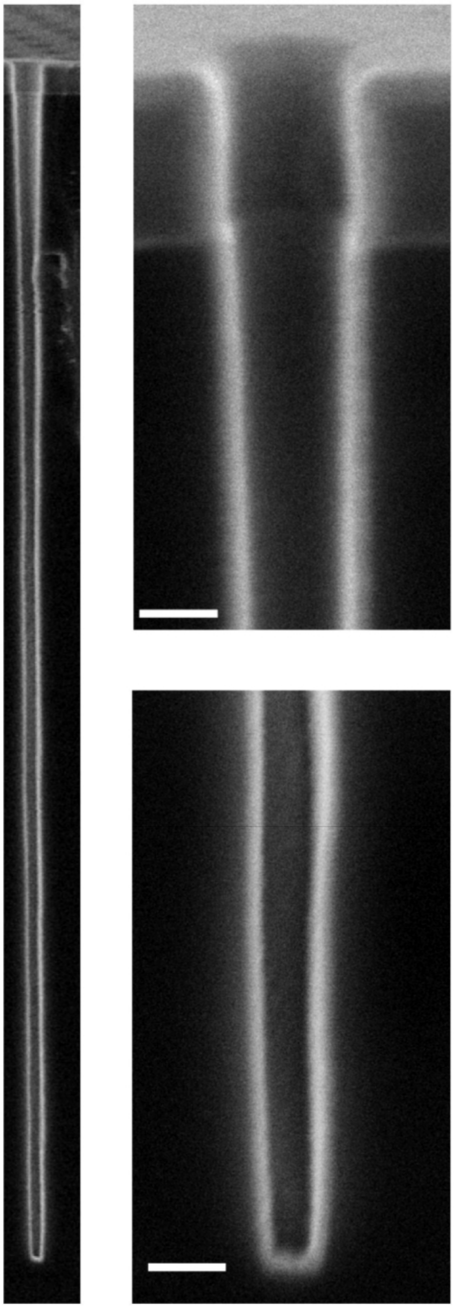

Fig. 3. SEM images of a coated high aspect ratio via. The white bar on the bottom of each image represents 100 nm.

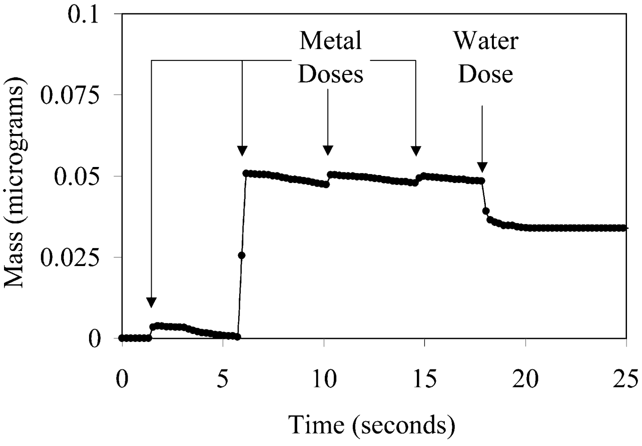

Fig. 4. The QCM mass changes during 1 ALD cycle using undersaturating doses of the tris(diethylamido)(ethylimido)tantalum precursor and water at 250 °C.

$Ta(NEt)(NEt_2)_3$ chemically adsorbs to the hydroxide-terminated surface with the concomitant breaking of metal–nitrogen bonds and the formation of metal–oxygen bonds. This first chemical adsorption reaction forms between two and three tantalum–oxygen bonds. In the second step water reacts with the surface bound metal amides to regenerate the surface hydroxyls by cleaving the remaining one or two tantalum–nitrogen bonds. Both steps release diethylamine and ethylamine as byproducts detected using ^{1}H-NMR of the effluent.

Electrical measurements were taken on samples ranging in thickness from 10 to 100 nm. Leakage current density was found to be consistently below 1 $\mu A/cm^2$ for an applied electric field of 1.5 MV/cm, which is significantly better than as-deposited films prepared by conventional CVD methods [11]. The breakdown field was determined to be consistently greater than 4.5 MV/cm. High frequency capacitance measurements (from 100 kHz to 1 mHz) gave a dielectric constant of 28 ± 1 with no detectable frequency dispersion. No dependence of the electrical properties on thickness was observed.

5. Discussion

The results reported here show that the alkyl-amides of tantalum provide convenient and effective ALD precursors for highly conformal thin films of tantalum(V) oxides. The reactions between the amide precursors and the surface are extremely rapid, irreversible and self-limiting. The films produced using the amide precursors exhibited a very high degree of conformality: 100% step coverage on holes with aspect ratios greater than 35. At deposition temperatures where precursor decomposition was not observed, films produced from both precursors were indistinguishable.

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