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Metallorganic chemical vapor deposition of Ta_2O_5 films

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Abstract

Ta_2O_5 films were grown by Pulsed-Metal Organic Chemical Vapor Deposition (Pulsed-MOCVD). This technique utilizes direct liquid injection of a precursor solution using an ultrasonic nozzle to introduce the precursor vapour into the low-pressure vertical cold-wall reactor. Tantalum (V) ethoxide ($C_{10}H_{25}O_5Ta$) was chosen as alkoxide because it is already an oxygen-containing precursor and its decomposition temperature is low. Films were grown in the temperature range 400–800 °C. Three solution concentrations were tested (1, 2 and 4 vol.%). Experimental results were analysed to determine the growth rate controlling mechanisms and film quality. The highest growth rate was achieved with the most dilute solution and film thickness of 3 μm was achieved with this technology with a growing rate of 8.52 μm/h. The refractive index and dielectric constant of the films increase with the growth in temperature, and as for the growing rate, the 1 vol.% solution leads to the best results. Analysis shows that the morphology and porosity of the films can be controlled by deposition temperature and solution concentration. Pulsed-MOCVD has demonstrated good performance with uniform film thickness and high growth rate.

Keywords: CVD; Dielectric properties; Films; Ta_2O_5

1. Introduction

The high rate deposition of dielectric films at low cost and low temperature is desirable in electronic and optical applications to increase the productivity and to fit the special requirements of the devices. For example, due to its wide field of applications in semiconductors, Ta_2O_5 has been extensively studied both experimentally and theoretically. In the last decade studies on Ta_2O_5 have been further motivated by the dramatic scaling down of silicon integrated circuits.

Ta_2O_5 can be employed as the dielectric layer for storage capacitors in DRAM's,[1,2] gate oxides in field effect transistors,[3] insulating layers in thin film electro luminescent devices,[4] sensor layers in chemical and biological environments,[5] optical wave guides,[6] thin film transistors and antireflection layers for silicon solar cells.[7]

Over the years a large number of deposition methods for Ta_2O_5 thin films have been used. Films can be deposited by anodic or thermal oxidation of Ta layers,[8] sputtering,[9] vacuum evaporation,[10] atomic layer deposition (ALD),[11] ion assisted deposition[12] and sol-gel methods[13] but the most commonly used processes are those based on CVD[14] which are currently considered as the standard method. All methods have some drawbacks. High oxidation rate can be obtained with anodic oxidation but the films generally contain a significant density of electron traps, which require annealing at high temperatures. During thermal oxidation atoms from the substrate can diffuse into Ta_2O_5 and oxidize. Using sputtering the film stoichiometry is rather difficult to control and the film density is low. When high vacuum and high-energy beams are used modification of the substrate microstructure can occur. Ion assisted deposition requires an electron beam bombardment and the depositing film is irradiated with low-energy O_2 ions. Sol-gel methods lead to porous films that contain a large amount of CH-based species. CVD methods can give uniform, conformal and adherent films, but the disadvantages of these methods are the manipulation of toxic, explosive or corrosive gases and the use of comparatively high temperatures (400–1100 °C). Moreover, carbon and hydrogen contaminants from the precursors lead to porous and

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defective oxide films and therefore to high leakage current densities. Many technological difficulties yielding low quality dielectrics remain unsolved. Leakage current is one of the most stringent performance parameters. Thermal stability is another important issue and processing costs are paramount, particularly in alternative energy and environmental technologies such as solar photovoltaic and electric automobiles, which must compete with established technologies.

The purpose of this paper is to design a low cost process for the deposition of oxide films (Ta_2O_5) on large metal substrates for dielectric applications and as an anti-reflective coating. Objectives will include characterization of growth rate, and microstructure of films prepared from candidate metalorganic precursors. At this stage the deposition will be carried out on flat substrates in the existing research-scale Pulsed-MOCVD system. The target technology for this process innovation is the dielectric layer for production of low-cost solar photovoltaic panels. For this purpose a Metal Organic Pulsed Chemical Vapor Deposition (Pulsed-MOCVD) technique will be tested. This technique utilizes direct liquid injection of a metered amount of precursor solution into a low-pressure reactor through an ultrasonic nozzle to provide small droplets, and the pulsing delivery of the liquid precursor. Experiments were conducted to evaluate the performance of the Pulsed-MOCVD process. A large number of experiments allowed us to determine the growth rate and film morphology throughout the range of deposition parameters (temperature, precursor concentration).

2. Experimental procedure

The Pulsed-MOCVD system, described in detail elsewhere,[15,16] utilizes direct liquid injection of a dilute precursor solution using an ultrasonic nozzle to introduce the precursor vapour into the low-pressure vertical cold-wall reactor (see Fig. 1). Tantalum (V) ethoxide ($C_{10}H_{25}O_5Ta$) was chosen as the alkoxide because it is already an oxygen-containing precursor and was exploited to deposit Ta_2O_5 films without supplementary oxygen sources. Moreover, Tantalum (V) ethoxide decomposes at relatively low temperatures ($>275\ ^\circ C$).[17] Solutions of a high volatility solvent, toluene, and up to 4 vol.% of alkoxide precursor, Tantalum (V) ethoxide, were prepared in a controlled atmosphere dry glove box. The desired solution was then loaded into the sealed precursor supply bottle and installed in the liquid supply system.

Fig. 1 shows a schematic drawing of the vertical cold-wall apparatus with 5 cm susceptor diameter. The pulsed liquid injection is accomplished by controlling the flow through three solenoid valves. Adjusting the concentration of the precursor in the solution further

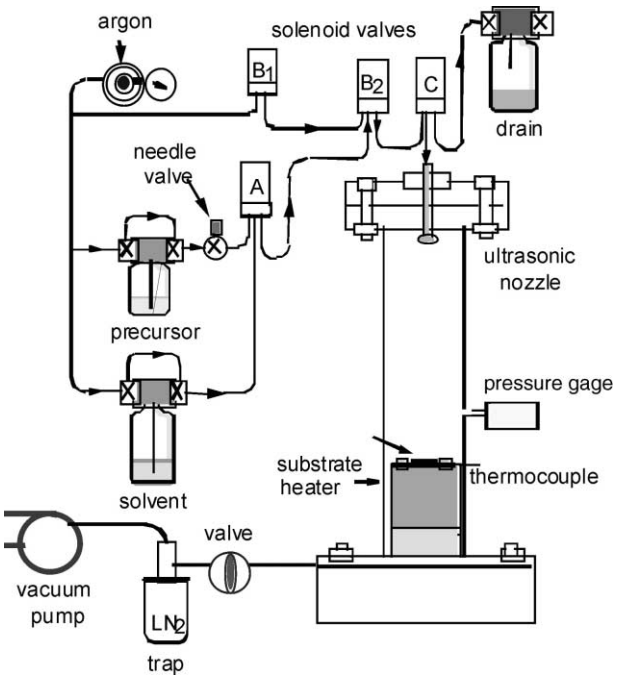

Fig. 1. Schematic drawing of Pulsed-MOCVD equipment with vertical cold-wall apparatus and 5 cm susceptor diameter.

controls the delivery of the precursor to the reactor. A halogen lamp was utilized for susceptor heating. The deposition temperature is measured and controlled by a thermocouple inserted into a cavity in the susceptor. The reactor pressure is provided by a rotary vacuum pump and the exhaust is captured in a liquid nitrogen trap.

The reactor was operated to maximize the precursor throughput while minimizing the impingement of droplets on reactor walls or the substrate. The pulse time, optimised for the reactor geometry and pump speed, was 14 s. Too short a pulse period does not provide sufficient vacuum and inhibits droplet evaporation. Sono-Tek Corp. piezoelectric transducers produce vibrations amplified through the horns, which are normal to the atomizing surface, setting up standing waves in the liquid supplied the nozzle. The height of the waves is sufficient to overcome the liquid surface tension and droplets are ejected. Droplets do not have an initial velocity and are subject only to gravitational acceleration. Substrates used were either nickel or alumina plates. Growth rate and morphology of the deposited films were studied over the range of the investigated deposition temperature and precursor concentration. The growth rate of the films was measured over the temperature range (500–800 °C). Growth rate measurements were accomplished by two methods, an in-situ colour fringe shift rate and post-deposition thickness measurement by ellipsometry. Ellipsometry was also used to characterize the film refractive index. Representative film surfaces and cross sections from each

range of deposition conditions were examined with an optical and a scanning electron microscope. The crystal structure of the films was determined by X-ray diffraction (Bruker D5005) and characterized by the Rietveld method for crystal structure refinement. CuK_α radiation was used. The surface morphology was also observed by atomic force microscopy (AFM). The dielectric constant was measured using a semiconductor parameter analyser (HP 4145B) and an LCR meter (HP-4284A) at a frequency of 1 MHz.

3. Results and discussion

Films were successfully deposited on both substrates throughout the range of temperature and precursor concentration. In Fig. 2 the deposition rate is plotted as a function of the temperature in the range from 500 to 800 °C for different metal organic precursor concentrations. As found in a previous paper using the same set-up but different kinds of films,[18] the curves show three stages: during stage I the growth rate follows an Arrhenius relationship and the activation energies were found to be 64.7, 49.9 and 47.1 kJ/mol for concentrations of 1, 2 and 4 vol.% of Ta (V) ethoxide, respectively. The Arrhenius behaviour suggests that the growth process is surface reaction limited. Stage II is a region in which the growth rate is temperature independent and in stage III the growth rates decreases with temperature. The decrease of the growth rate observed during phase III occurs because the deposition rate becomes limited by droplet evaporation.

Stage II is the regime of engineering interest and from Fig. 2 it is clear that it is reached at lower temperatures for the solution with 1 vol.% of Ta (V) ethoxide. Using this solution films as thick as 3 μm were deposited with a growing rate of 8.52 μm/h.

The crystalline phases of all films were examined with a conventional X-ray diffractometer and characterized by the Rietveld method for crystal structure refinement. Fig. 3 shows the XRD pattern of a film deposited on a Ni substrate. The films (a), (b) and (c) were prepared at substrate temperatures of 500, 600 and 700 °C, respectively. Below 600 °C the diffraction pattern consisted of a diffuse diffraction curve. Such a profile is an indication of an amorphous-like structure. For temperatures higher than 600 °C the crystalline phase starts to form and was identified as the single orthorhombic β-Ta_2O_5 phase.

The SEM micrographs of the film on alumina substrates are shown in Figs. 4 and 5. From cross-section views there is no indication of an interface, demonstrating that the layer had a good coherency to the substrate.

Although homogeneous films were deposited, pinholes were observed on films. The pinholes were possibly the result of small particles that were present in the reaction chamber or the formation of porous films.

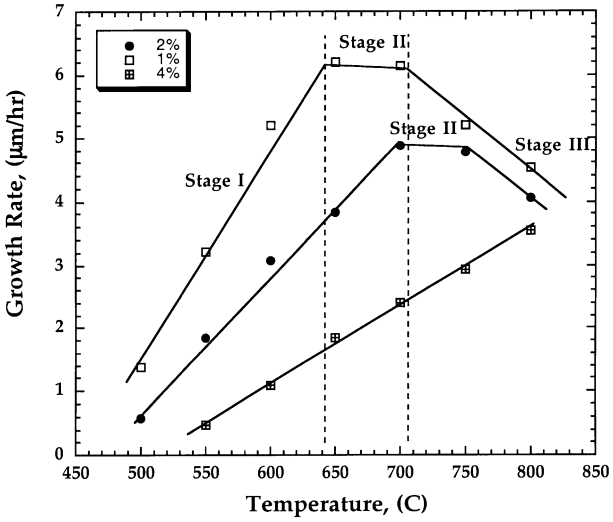

Fig. 2. Deposition rate plotted as a function of the growth temperature for different metal organic precursor concentrations.

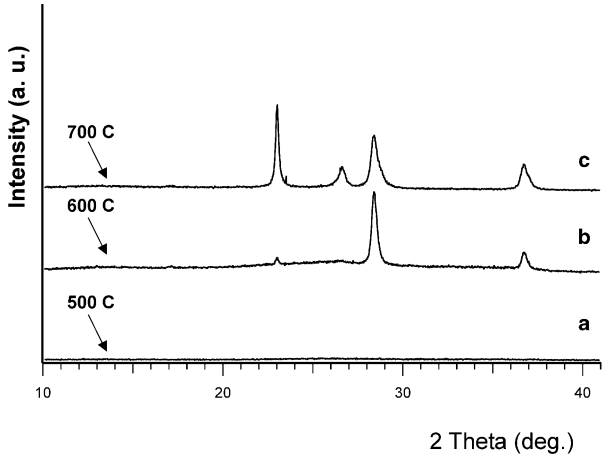

Fig. 3. XRD pattern of the film deposited on Ni substrates. Below 600 °C the films have an amorphous-like structure. For temperatures higher than 600 °C the crystalline orthorhombic β-Ta_2O_5 phase starts to form.

The refractive index n values were 1.97, 2.03 and 2.07 for films deposited from solutions with 4, 2 and 1 vol.% of Ta (V) ethoxide, respectively. Therefore the films deposited from the solution with 1 vol.% of metallic precursor are denser.

AFM analysis of the Ta_2O_5 films showed that the surface is smooth and for films grown at 650 °C from a 1 vol.% of Ta (v) ethoxide precoursor the root mean square (RMS) roughness was 0.9 nm although the presence of few pinholes was evident.

It was found that the dielectric constant critically depends on whether the crystalline phase has formed. Fig. 6 is the dielectric constant plotted as a function of the deposition temperature. The film thickness was 1.3 μm.

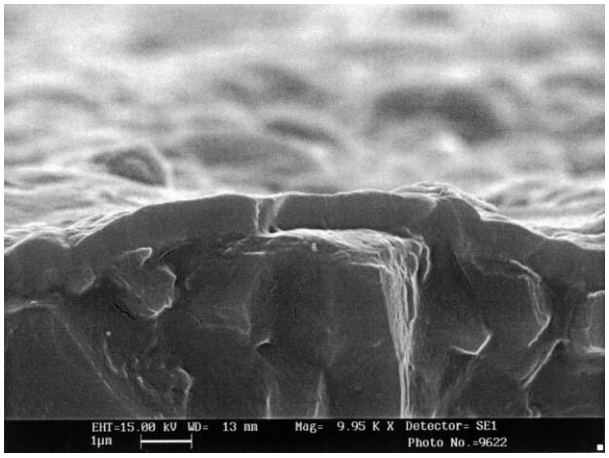

Fig. 4. SEM micrographs of a cross-section of a Ta_2O_5 film on alumina substrate (from 1 vol.% of metal organic precursor solution).

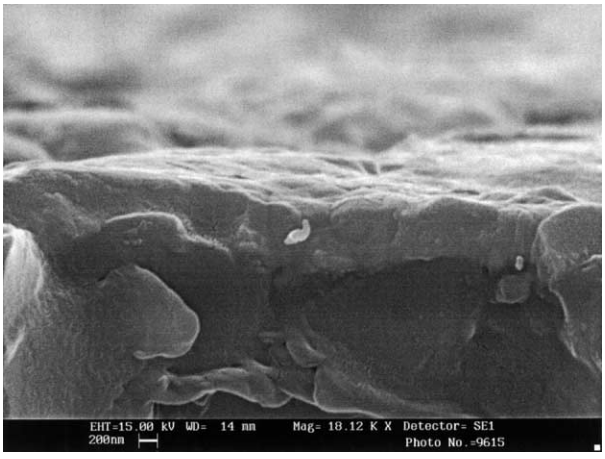

Fig. 5. SEM micrographs of a cross-section of a Ta_2O_5 film on alumina substrate (from 2 vol.% of metal organic precursor solution).

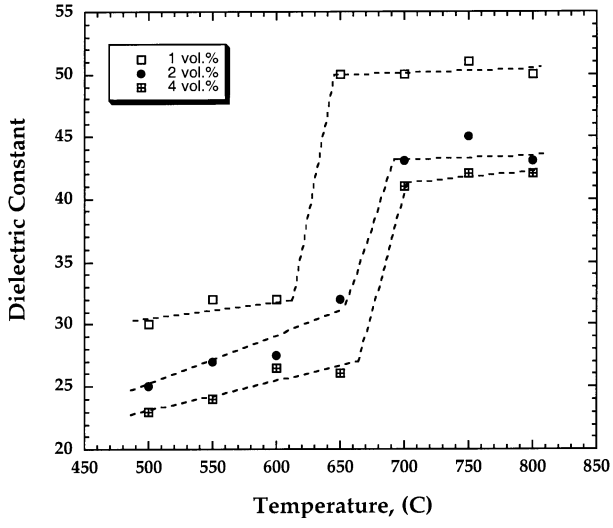

Fig. 6. Films dielectric constant plotted as a function of the deposition temperature.

As shown in the figure, the dielectric constant remains low and practically unchanged for films deposited at temperatures up to 600 °C however the dielectric constant raised for deposition temperatures higher than 650 °C.

4. Conclusions

The results of the experiments demonstrate that the Pulsed-MOCVD system can be effectively used to deposit tantalia films on metal or alumina substrates using liquid alkoxide precursors. The pulsed injection delivery system provides a unique mass transfer regime and high growth rates. Growth rates up to 8.52 μm/h were achieved for Ta_2O_5 deposition using a solution of 1 vol.% of Ta (V) ethoxide precoursor.

The unique reactor flow conditions that result from pulsing the liquid precursor supply result in high mass transfer rates to the deposition surface and good uniformity in the film. The Pulsed-MOCVD system produces films with coverage and uniform thickness usually found in low-pressure systems. However, because of the high precursor vapour concentration in the first part of each pulse the overall growth rates are relatively high.

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