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Nanomechanical properties of platinum thin films synthesized by atomic layer deposition

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ABSTRACT

The nanomechanical properties of Pt thin films grown on Si (100) using atomic layer deposition (ALD) were investigated using nanoindentation. Recently, atomic layer deposition (ALD) has successfully demonstrated the capability to deposit ultra-thin films of platinum (Pt). Using (methylcyclopentadienyl) trimethylplatinum ($MeCpPtMe_3$) as chemical platinum precursor and oxygen (O_2) as the oxidizing agent, the ALD synthesis of Pt can be achieved with high conformity and excellent film uniformity. The ALD process window for Pt films was experimentally established in the temperature range between 270 °C and 320 °C, where the sheet conductance was constant over that temperature range, indicating stable ALD Pt film growth rate. ALD growth of Pt films exhibits very poor nucleation and adhesion characteristics on bare Si surfaces when the native oxide was removed by 2% HF etch. Pt adhesion improves for thermally oxidized Si wafers and for Si wafers covered with native oxide. Three ALD Pt films deposited at 800, 900, and 1000 ALD deposition cycles were tested for the structural and mechanical properties. Additionally, the sample with 900 ALD deposition cycles was further annealed in forming gas (95% N_2 and 5% H_2) at 450 °C for 30 min in order to passivate dangling bonds in the grain boundaries of the polycrystalline Pt film. Cross-sectional transmission electron microscopy (TEM), X-ray diffraction (XRD), atomic force microscopy (AFM), and scanning electron microscope (SEM) were employed to characterize the films' surface structure and morphology. Nanoindentation technique was used to evaluate the hardness and modulus of the ALD Pt films of various film thicknesses. The results indicate that the films depict comparable hardness and modulus results; however, the 800 and 1000 ALD deposition cycles films without forming gas annealing experienced significant amount of pileup, whereas the 900 ALD deposition cycles sample annealed in forming gas resulted in a smaller pileup.

1. Introduction

Thin films and coatings of the noble metal platinum (Pt) have found numerous applications in catalysis and microelectronics due to their excellent electrical properties and chemical stability. For example, platinum is used as electrode at high temperature in oxidative and reductive environments. The main applications of Pt films are found in the automotive industry, where it is used in catalytic converters for vehicle emissions control devices. In terms of consumption levels of bulk Pt, the jewelry industry and the watch industry is in second place following the automotive industry. Platinum is also heavily used for electrodes, anticancer drugs, oxygen sensors, high-end spark plugs coatings, and turbine engines. Platinum can be used as electrodes at high temperatures in harsh conditions such as oxidizing and reducing environments [1] because of its excellent chemical stability. Furthermore, Pt is also widely used in fuel cells due to its good catalytic activity for O_2 reduction and H_2 oxidation reactions at the electrode/electrolyte interface [2]. Due to its chemical stability and high melting point, Pt provides a suitable structure for temperature sensors [3]. In chemical engineering Pt coatings are utilized as catalyst to enhance a multitude of chemical reactions. Platinum films are also applicable as a gate metal with high-k dielectrics in metal-oxide-semiconductor field effect transistors (MOSFETs) because of its high work function [4–6]. Some of the early work on atomic layer deposition (ALD) synthesis of platinum films has been reported at the university of Helsinki in Finland in 2003 [7]. Since then several research groups have followed up the ALD investigations in more detail [8–12] and also looked into selective ALD of Pt [13]. However, little literature has been devoted to the nanomechanical properties of ALD Pt thin films. In contrast to bulk platinum, a good understanding of the nanomechanical properties of ultra-thin ALD films of Pt is still lacking. This study was devoted to the nanomechanical analysis using an XP nanoindenter from Agilent Technologies in order to measure the hardness and modulus of the resulting ALD Pt thin films.

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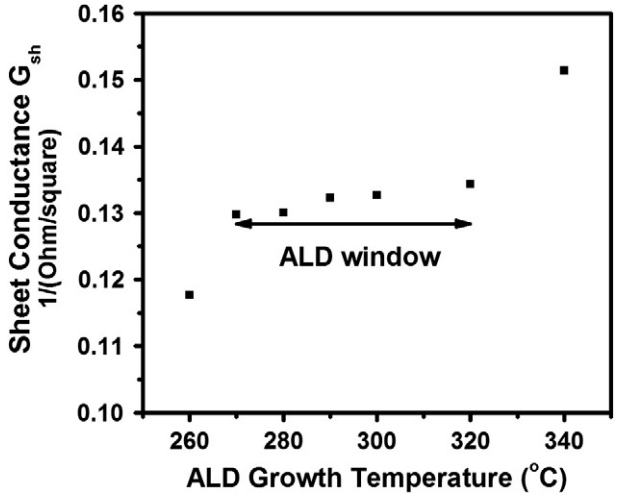

Fig. 1. Sheet conductance of as-deposited Pt film as a function of growth temperature for 400 ALD cycles to establish the process window of stable Pt growth.

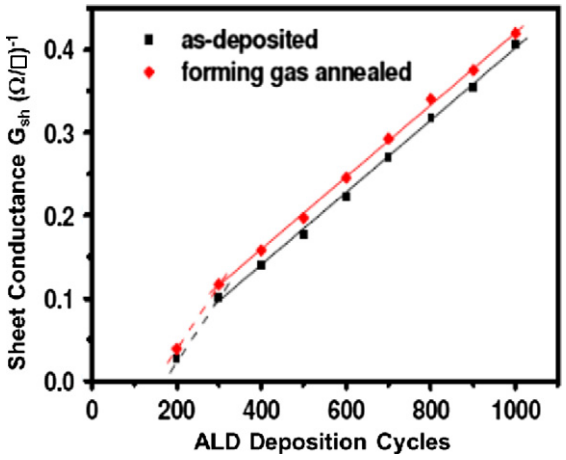

Fig. 2. Electrical measurements of sheet conductance G_{sh} of Pt films exhibit good linear relationship as a function of the number of ALD deposition cycles.

2. Experiment details

Among the thin film growth techniques, the ALD technology provides unique features such as precise control of thin films with atomic resolution, high uniformity, good conformality, surface saturating property, self-limited reactions and high aspect ratio. After the initial nucleation phase the film thickness in an ALD deposition is linearly dependent on the number of ALD deposition cycles used. Each ALD cycle is composed of exposing the substrate in the ALD reaction chamber to the first chemical precursor, followed by purging the chamber with inert gas (e.g., Ar, N_2), and then finally reacting precursor 2 with precursor 1 in order to synthesize the desired thin film material. This last step is followed by purging with N_2.

In this study, we investigated the initial stages of the nucleation process of ALD Pt thin films and the synthesis of Pt nanotube structures with high aspect ratio using the metal organic compound (methylcyclopentadienyl) trimethylplatinum ($MeCpPtMe_3$) and oxygen as the chemical ALD precursors.

Atomic layer deposition (ALD) technology utilizing the Cambridge Nanotech Savannah 100 cross-flow ALD reactor was used to deposit thin films of platinum with angstrom resolution. Noble metal thin films of platinum were deposited on four inch wafers of p-type boron doped Si (100) substrates. The ALD Pt thin films were initially grown on Si substrates to analyze the film growth mechanism and the electrical properties. For platinum (Pt) deposition, (methylcyclopentadienyl)trimethylplatinum ($Me_3CpPtMe_3$) chemical precursor was used for ALD precursor 1 and oxygen (O_2) for ALD precursor 2. For chemical precursor 1, the metal organic compound $MeCpPtMe_3$ was heated to 80 °C in order to generate sufficient vapor pressure. By investigating various deposition temperatures with the ALD precursor cylinder containing $MePtCpMe_3$ heated at 80 °C, we established the following ALD Pt film growth rates of 0.050, 0.017, and 0.330 Å/cycle at 150 °C, 200 °C, and 270 °C deposition temperature. For the early process window experiments, the $Me_3CpPtMe_3$ vapor was allowed to enter the ALD reaction chamber for a pulse duration of 0.25 s. The O_2 pulse duration for the ALD precursor 2 was set to 0.5 s. The two ALD precursor vapor pulses were separated by 5 s of N_2 purging pump time and the ALD chamber pressure was held at 13.33 Pa. The purging gas was N_2 and the N_2 flow rate was set at 20 sccm. For the

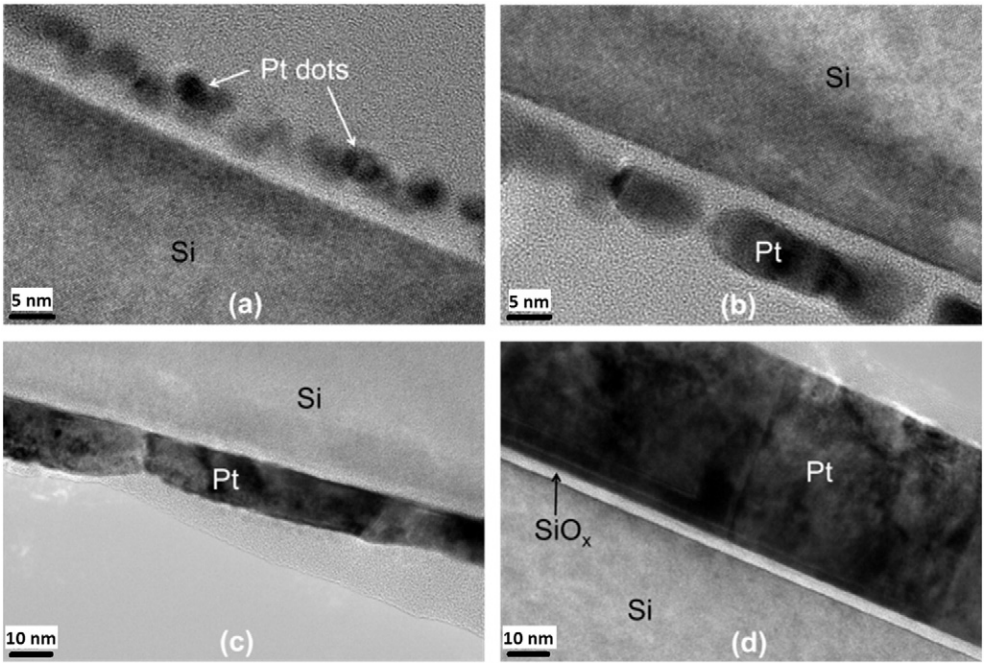

Fig. 3. TEM cross-sections of ALD depositions of Pt at 300 °C for different thickness stage: (a) 50 ALD cycles, (b) 100 ALD cycles, (c) 200 ALD cycles, and (d) 1000 ALD cycles.