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Platinum thin films with good thermal and chemical stability fabricated by inductively coupled plasma-enhanced atomic layer deposition at low temperatures

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ABSTRACT

The inductively coupled plasma-enhanced atomic layer deposition (PEALD) method was used to fabricate ultrathin and smooth Pt thin films at low temperatures without the use of a Pt seed layer. The Pt thin metal films deposited at 200 °C onto Si and glass substrates exhibited high conductivities (<12 μΩ cm for films with a thickness greater than 8 nm) and thermal stabilities resembling those of the bulk material. The measured density of the deposited Pt thin films was 20.7 ± 6 g/cm^3. X-ray photoelectron spectra of the films showed clear 4f peaks (74.3 eV ($4f_{5/2}$) and 71.1 eV ($4f_{7/2}$)), and X-ray diffraction measurements showed the (111) peak of the fcc structure. The deposited Pt layers were in crystal form. The 25.5-nm Pt films coated onto 170-nm-wide trench structures (aspect ratio of 3.5:1) exhibited good step coverage. The PEALD-deposited Pt thin films were chemically stable under high-temperature light illumination and could serve as catalysts under strongly alkaline conditions (pH = 12) during the long-term oxidization of ammonium ions.

1. Introduction

The inductively coupled plasma-enhanced atomic layer deposition (PEALD) method is a useful atomic-layer deposition (ALD) technology that incorporates a powerful inductively coupled plasma generator. In ALD methods, thin films of crystalline materials are grown one atomic layer at a time [1]. Alternate pulsing of precursor gases and vapors onto the substrate surface leads to subsequent chemisorption and surface reaction of the precursors [2]. A self-limiting growth mechanism facilitates the growth of conformal thin films over large areas with an accurate thickness in each deposition cycle [3]. Various dielectric materials have been deposited using these technologies, including Al_2O_3 [3–5], polycrystalline luminescent ZnS:Mn [6], TiO_2 [7, 8], TaN_x [9, 10], ZrO_2 [11], and ZnO [12]. Many types of metals have also been deposited with these technologies, including Ru [13, 14], Pt [15–18], and Cu [19].

Materials with high dielectric constants (HfO_2, Al_2O_3, TiO_2, etc.) have been deposited using conventional thermal ALD systems [20–22]. Recently, Pt films were deposited onto TaN_x by a thermal ALD method with a seed/barrier stack and exhibited good step coverage [10]. Various Pt precursors, such as (methylcyclopentadienyl)trimethylplatinum ($MeCpPtMe_3$) and $Pt(acac)_2$ (acac = acetylacetonate), have been used to prepare Pt films using the ALD method. In the thermal ALD of Pt, reactions are confined to a limited number of reactive sites on the SiO_2 substrate, thereby forming isolated Pt nanoparticles (NPs). The uniform Pt NPs were deposited at a high substrate temperature of 300 °C using the precursor $MeCpPtMe_3$ and oxygen [10, 18, 23]. When the cycle number of ALD was increased, the Pt NPs became larger and then coalesced to form a rough film. Only PtOx films were obtained by the combination of $Pt(acac)_2$ with O_3 at a low substrate temperature of 130 °C. Thus, thin Pt layers are not easily fabricated.

In semiconductor fabrication, inductively coupled plasma is essential in dry etching in order to construct specific structures on InP, Si, etc. Inductively coupled plasma has also been applied to mass spectrometry and to the fabrication of carbon nanowalls, graphenes, GaN nanorods, etc. In recent years, the PEALD method has been used to fabricate metal nitrides and metal films with high conductivity. This deposition process was developed for microelectronic applications such as large-scale film deposition [9, 13, 14, 19, 24, 25] or plasmonic oxidization of ammonium [26, 27]. A ruthenium buffer layer was deposited at 270 °C to improve adhesion while not degrading the film resistivity of Cu. Tantalum nitrides have been deposited as strong diffusion barriers at sub-nanometer thicknesses. Cu has been deposited using hydrogen plasma substrate pretreatments. The PEALD method was used to improve Cu nucleation and to enable lower resistivity.

Pt thin films exhibit high chemical stability, high thermal stability, and excellent electrical conductivity, which make them potentially useful in numerous applications. In this study, we demonstrate how to fabricate thin metal films by the PEALD method. The Pt metal thin films deposited by the PEALD method are thin, smooth, and exhibit high

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conductivity that approaches that of the bulk material. Deposited Pt films also exhibit high thermal stability and good durability under harsh environments. The deposition of these films by the PEALD method shows great promise for the development of various advanced applications.

2. Experimental details

Thin homogeneous Pt films were deposited onto Si substrates, 170-nm-wide trench structures, and glass substrates using high-energy reductive plasma enhanced deposition in a home-built PEALD system without the use of a Pt seed layer (Fig. 1) [26–28]. Alternate pulsing of the precursor gases and vapors onto the substrate surface leads to subsequent chemisorption and surface reaction of the precursors [2]. First, the vertical flow method was used to introduce the ALD reactants of the precursor vapor into the chamber to react on the substrate. Second, the purge gas (N_2) was introduced to remove volatile byproducts from the process chamber. Third, the O_2 plasma source was generated at 13.56 MHz in a radio frequency (RF) matching box. Plasma is composed of charge carriers of ionized molecules or atoms that can be controlled via the application of electromagnetic fields. The growth mechanism of thin Pt films and their quality depend on the pressure and the plasma exposure time [17]. To avoid chemical vapor deposition, we used an automated shutter in the PEALD process to independently control the O_2 plasma exposure time and the Pt precursor injection-pulse time [28]. Fourth, the purge gas (N_2) was introduced to remove volatile byproducts from the process chamber. In this ALD method, the complete processing cycle leads to a self-limiting surface and provides excellent control of the atomic layer thickness and good step coverage in ultrahigh-aspect-ratio trench structures. To increase the thickness of the thin film, we repeated the reaction cycles a predetermined number of times [29].

The plasma chamber of the home-built PEALD system consists of a quartz tube connected to an inductively coupled plasma source. A remote-controlled and built-in shutter allows the induced plasma gases to enter the deposition chamber only during controlled periods of time. The plasma generated from $MeCpPtMe_3$ (Sigma-Aldrich, purity 98%) mixed with Ar/O_2 was used as the Pt precursor. For all PEALD processes, the plasma generating power was 400 W. The Ar and O_2 pressures were 40 and 13.3 Pa, respectively. The $MeCpPtMe_3$ precursor vapor was generated at 70 °C and was injected in predetermined pulses times of 0.2 to 0.5 s. The Ar/O_2 plasma exposure time was 3 s. The growth temperatures for various samples on the target substrate ranged from 100 °C to 200 °C. At the end of each cycle, the purge gas (N_2) (99.9995%) was introduced in 5-s pulses. Herein, we measured the characteristics of the Pt layers deposited onto a Si (100) substrate with a native oxide layer and the Pt layers deposited onto glass substrates.

The crystal structure of the deposited layers was analyzed by low-angle (<2°) X-ray diffraction on a diffractometer equipped with an 18-kW rotating anode X-ray source (XRD: Rigaku TTRAX III). X-ray photoelectron spectroscopy with a Schottky thermal field emitter (XPS: Perkin Elmer PHI 670) was performed using an ESCA PHI 1600 spectrometer. The film morphology and thickness were observed by transmission electron microscopy (TEM) using a JEOL JEM-2100F transmission electron microscope operated at an accelerating voltage of 160–200 kV). Surface roughness was measured by atomic force microscopy (AFM, Veeco Dimension 3100, processed in tapping mode), and the resistivity was measured using a Hall-effect measurement system (Accent/HL 5500PC). The X-ray reflectivity measurements using an 18-kW rotating anode X-ray source (XRR, Rigaku TTRAX III) were used to measure the deposited thickness and density of the Pt thin films.

3. Results and discussion

Pt films were deposited by the PEALD method at low growth temperatures from 100 °C to 200 °C under various reaction conditions without the use of a Pt seed layer. The self-limiting reactions ensure that the film thickness increases cycle by cycle. The Pt film growth rate was approximately 0.4 Å per cycle. At growth temperatures of 175 °C and 200 °C with an $MeCpPtMe_3$ injection pulse time of 0.5 s, XPS (Fig. 2(a)) measurements calibrated with respect to carbon 1s (285.5 eV) revealed a Pt doublet peak representing bonding energies of 74.3 eV ($4f_{5/2}$) and 71.1 eV ($4f_{7/2}$); these peaks resemble those reported elsewhere for Pt films [30]. The Pt thin films exhibited a high-intensity preferred-orientation (111) peak [fcc structure, Fig. 2(b)], as previously reported by other authors [17, 18]. The Pt (111) diffraction peak was observed when the substrate temperatures during fabrication exceeded 175 °C. The polycrystalline Pt complex layer was deposited at a substrate temperature of 100 °C. A smooth Pt thin film was formed at a substrate temperature of 200 °C. The deposition process at a growth temperature of 200 °C resulted in the deposition of 8-nm Pt films.

For the Pt oxide films (8 nm) deposited at 100 °C without the use of a Pt seed layer, the high-resolution transmission electron microscopy (HRTEM) micrograph in Fig. 2(c) shows that the microstructure of the

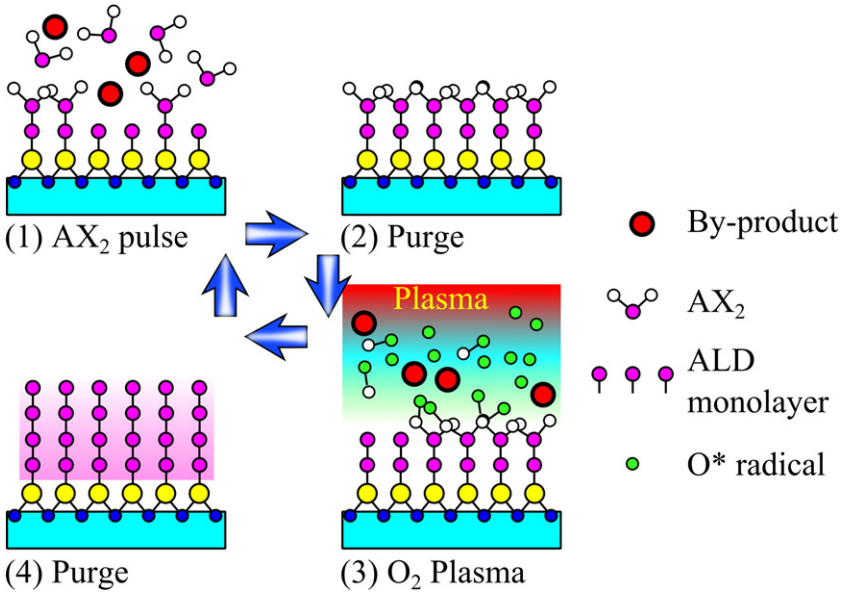

Fig. 1. (color online) Schematics of the reaction process in plasma-enhanced atomic layer deposition [28].