Thin Solid Films 640 (2017) 116–122

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Qualifying ultrathin alumina film prepared by plasma-enhance atomic layer deposition under low temperature operation

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ARTICLE INFO

Keywords:
Plasma-enhanced atomic layer deposition
Alumina
Raman spectroscopy
X-ray diffraction
Transmission electron microscopy

ABSTRACT

Preparation of ultrathin alumina (Al_2O_3) films through Plasma-Enhanced Atomic Layer Deposition (PE-ALD) at low substrate temperature is discussed. The present work aims to investigate the physical mechanism of the PE-ALD deposition process and also the characteristics of the ultrathin alumina films on silicon 〈100〉 wafer deposited using the technique. The deposition was performed using trimethyl aluminum (Al $(CH_3)_3$) as the precursor and argon gas for purging. During deposition, the target temperature was kept constant at ~80, 100 and 150 °C and the pressure was $\sim 1.3 \times 10^{-2}$ Pa. Two deposition cycles were tested, 400 and 800 cycles. As for understanding the process, the films deposited with and without oxygen plasma were compared. Various thin film characterization techniques, including Atomic Force Microscope (AFM), ellipsometry, Raman spectrometry measurement, X-ray diffraction (XRD), and indentation technique, were applied for investigating the film properties. A transmission electron microscope (TEM) equipped with high-angle annular dark-field imaging line scan modes and energy-dispersive X-ray spectroscopy acquisition was used for imaging thin film cross-sections. We found that the number of deposition cycles did not affect the substrate surface roughness as evidenced by AFM images. The mechanical property, the hardness of the film deposited with 800 cycles and plasma was the best. Raman spectroscopy measurements showed that a Al-O-Si phase exists when the films were deposited at 100 °C and 150 °C for 400 and 800 cycles under oxygen plasma atmosphere. While no Al-O-Si phase existed after the same number of ALD deposition cycle without plasma. Results from XRD measurements indicated that the films deposited at 100 °C and 150 °C for 400 and 800 cycles under oxygen plasma atmosphere has an Al-O structure. TEM images clearly displayed the interface between the thin films, SiO_2 interface layers and Si substrates. As for the sample deposited at 80 °C, an Al_2O_3 film was hardly seen, but when increasing the deposition temperature to 100 °C and 150°, films started to build on top of the substrate. However, for all deposition conditions, TEM revealed that the amounts of carbon atoms in the reaction site remained relatively high.

1. Introduction

As technology trends to downscale and miniaturization to the atomic-level, thin film technology is required for various applications. Atomic layer deposition (ALD) is one of the promising methods as it enables to deposit a variety of materials from pure metal to oxide, nitrites and polymers to various substrates materials for industrial requirements at relatively low temperature [1,2]. A film structure deposited by the technique appears to be a unique feature over other techniques, such as improvement in film quality, better step coverage, better controlling stoichiometry of films at the angstrom level, and pin hole free [3,4]. Advanced applications for industry are, for example, coating protection of magnetic recording heads for hard disk drives, protective coating of micro-electro mechanical systems, gate insulators, capacitors, barrier, solar cells, optical device, electro–luminescent devices, and thin film transistor [5].

ALD technique is a modification of the chemical vapor deposition technique (CVD). A film is grown on a substrate by exposing to sequential, non-overlapping pulses of alternate gaseous species (typically referred to as precursors). The technique is self-limiting, and these individual gas-surface reactions are called “half-reactions” [6]. The basic steps of ALD cycles consist of four steps [7]: the first precursor (precursor A) adsorbs on substrate surface forming one monolayer that chemisorbs to the surface. The second step is passing the purging gases

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http://dx.doi.org/10.1016/j.tsf.2017.09.008
Received 1 September 2016; Received in revised form 6 September 2017; Accepted 6 September 2017
Available online 07 September 2017

(nitrogen or argon) or evacuating the chamber, to remove the non-reacted precursor and the byproducts out of the chamber. Meanwhile, for the third step, a second precursor (precursor B) reacts with the chemisorbed molecules on the surface until saturation. The fourth step is passing the purging gases or evacuating the chamber again, to remove the non-reacted precursors and the byproducts out of the chamber. The most commonly used ALD for alumina (Al_2O_3) thin film deposition is thermal ALD (T-ALD), in which alternating pulsed of trimethyl aluminum (TMA) as metal source and water as oxygen source, facilitated with the substrate temperature as low as 250 °C [1,6,8]. Recently, plasma-enhanced ALD (PE-ALD) in which water is replaced by a plasma exposure as the oxygen source has been extensively study [1,5].

PE-ALD introduces the plasma to support chemical reactions in the chamber. The key success of the plasma during the thin film synthesis relates to the reactive species that are generated in the gas phase. Typically, the plasma supplies a low heat flux to the surface, and at the same time, additional energy could be provided to the deposition surface by the ion bombardment [5]. The energy provided by adsorbed species promotes the surface mobility, thus increasing film density, reducing interface structure and defect density between film materials and the substrate. Because of the higher reactivity of using the plasma generating oxygen radicals, PE-ALD has several capabilities over T-ALD, such as improved film quality and increased flexibility in process conditions [5,9], and in particular, can perform at lower substrate temperatures due to lower impurity levels [8,9].

Al_2O_3 film is an important protection layer because of its excellent dielectric property, high hardness, good adhesion to various surfaces, with good thermal and chemical stability. Al_2O_3 metastable polymorphs exist in many forms in which different phases have different properties [10]. α-Al_2O_3 film was mainly selected for high temperature applications such as steel and cutting tools because of its high thermal resistance and excellent mechanical properties [10]. κ-Al_2O_3 film can enhance wear resistance for high temperature applications, due to its high hardness, as an alternative to α-Al_2O_3 [11]. γ-Al_2O_3 film with low surface energy property is used as a catalyst due to its large surface area [10].

The present study aims to investigate the ultrathin alumina film property deposited by PE-ALD technique on silicon 〈100〉 wafer, mainly for mechanical property applications. In the investigation, the self-constructed PE-ALD system was employed. Each deposition used trimethyl aluminum (Al $(CH_3)_3$) as a precursor, argon gases for purging, and oxygen plasma as the oxidant. The film properties were investigated using various analytic techniques, including Atomic Force Microscopy (AFM), Spectroscopic Ellipsometry (SE), Raman Spectroscopy, X-ray diffraction (XRD) and Nanoindentaion measurement. As known, transmission electron microscopy (TEM), a microscopy technique in which a beam of electrons is transmitted through an ultra-thin specimen and interact with the specimen as it passes through it, is capable of imaging at a very high resolution and enables the user to examine fine details - even as small as a single column of atoms. TEM is also equipped with a Gatan Imaging Filter (GIF) which permits energy-filtered imaging and an energy dispersive x-ray spectrometer (EDS) which permits qualitative analysis. Therefore, thin Al_2O_3 deposited by PE-ALD is a good practice for TEM measurement, and the film information will be useful for the understanding of the deposition mechanism and also ease for deconvolution of results from other measurement techniques. Hence, physical mechanism underlying the PE-ALD technique can be drawn using these analytical techniques.

2. Experiment

The PE-ALD system used in this experiment was developed by the Plasma and Beam Physics Research Facilities, Chiang Mai University, Thailand, as shown in the schematic diagram in Fig. 1. The system consists of three sub-systems, i.e. precursor feeder system, microwave remote plasma, and control system [12]. The system consists of three mass flow controllers supplying gases for three functions of reaction. The first function uses argon gas as purging of the chamber. It also becomes a carrier gas of trimethyl aluminum (TMA), the 1st precursor, to transition phase, convergence from the liquid phase to the vapor phase of the precursor. The last function uses oxygen, the 2nd precursor, to generate plasma for oxidation of the films during deposition. The microwave remote plasma system is used to generate the dense plasma in the source tube, which is mounted on top of the chamber and propagates to the reaction chamber. In the present set-up, additional multicusp (or magnetic multipole) improves the plasma density by creating a magnetic line wall to protect the discharge anode and maintain a large volume discharge that makes the high-density and controllable plasma. The pressure between the plasma source tube and reactor chamber was maintained at $\sim 1.3 \times 10^{-2}$ Pa. The main system of the PE-ALD is controlled by the controller system. It connects and synchronizes all mass flow, providing various experimental schemes such as a different number of cycles and ranges of precursor (TMA, O_2 and Argon-purge) during ALD deposition.

The substrates, Si (1 − 0 − 0) wafers, were cleaned by the standard RCA technique with IPA and dried with nitrogen (N_2) before subsequently loaded to the deposition chamber. Alumina films were deposited with TMA and oxygen plasma, including argon gas as purging agent and carrier TMA. Prior to a deposition, the chamber was purged by argon gas for 10 min. One cycle deposition consists of 2 s TMA pulse, 1 s argon purge, 4 s O_2 pulse and 1 s argon purge. The flow rates of TMA and O_2-plasma were 1.0 and 7.5 SCCM, respectively, and Ar purge was 1.5 SCCM. The deposition cycle set-up is showed in Fig. 2.

In the first part, the study involved the investigation of the effects of deposition cycles on film properties, between 400 and 800 cycles. For comparison purpose, the depositions were done with and without oxygen plasma assistance. Further study focused on the investigation of the effects of the reaction temperature on the properties of the films. In this series, substrate temperatures during deposition were controlled to 80 °C, 100 °C, and 150 °C and the deposition was done with plasma assistance of 800 cycles. During deposition, the pressure was maintained at $\sim 3.07 \times 10^{-2}$ Pa. No post-treatments were deliberately done for all samples after deposition.

Several characterization techniques were applied to qualify the film properties. The surface roughness of the sample was evaluated using Atomic Force Microscope (AFM) (Bruker's Dimension Icon®) under the tapping mode to a scanning size of $\sim 1 \times 1\ \mu m^2$. The thickness of the film was determined by M-2000 Ellipsometer (J.A Woollam Co. Ellipsometry Solution). Nanoindentation (Hysitron) using Berkovich tip under 70 and 100 μN forces was applied to investigate the film hardness. A Jobin Yvon spectrometer HORIBA (T64000), equipped with triple monochromator, 532 nm solid state excitation laser, and a focused spot size of about 0.8 μm by a 100 × objective (NA = 0.9), was used for the Raman measurements. Crystalline phase and structure of film materials were monitored by the Advance X-ray diffractometer (Bruker D8), and the spectra were recorded over 10–80° 2 theta. Note that for comparison, in some measurements, the natural sapphire, a crystalline form of Al_2O_3, was also characterized by the same condition and it was denoted as the “standard alumina sample” in the discussion throughout the paper.

The chemical and morphological properties of films were investigated by TEM using FEI Osiris with super X-EDS Bruker Nano GmbH, Germany. Prior to measurement, the samples were coated with CrO_2 and cut into a lamellae shape by using the Focus Ion beam (FIB) samples preparation milling. Images were done using an energetic 200 keV electron beam under the mapping parameters; width 200 pixels, 11 nm; height 300 pixels, 17 nm; and pixels size 57 pm with TEM BF Image and high-angle annular dark-field imaging (HAADF) line scan modes.