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Comparing XPS on bare and capped ZrN films grown by plasma enhanced ALD: Effect of ambient oxidation

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ABSTRACT

In this article we compare x-ray photoelectron spectroscopy (XPS) measurements on bare- and capped-zirconium nitride (ZrN) films to investigate the effect of ambient sample oxidation on the detected bound O in the form of oxide ZrO_2 and/or oxynitride ZrO_xN_y. ZrN films in both bare- and Al_2O_3/AlN capped-XPS samples were grown by plasma-enhanced atomic layer deposition (PEALD) technique using tetrakis dimethylamino zirconium (TDMAZr) precursor, forming gas (5% H_2, rest N_2) inductively coupled plasma (ICP), and as received research grade process gases under identical process conditions. Capped samples were prepared by depositing 1 nm thick PEALD AlN on ZrN, followed by additional deposition of 1 nm thick ALD Al_2O_3, without venting of ALD reactor. On bare ZrN sample at room temperature, spectroscopic ellipsometry (SE) measurements with increasing ambient exposure times (t_{exp}) showed a self-limiting surface oxidation with the oxide thickness (d_{ox}) approaching 3.7 ± 0.02 nm for $t_{exp} > 120$ min. In XPS data measured prior to sample sputtering ($t_{sput} = 0$), ZrO_2 and ZrO_xN_y were detected in bare- samples, whereas only ZrN and Al_2O_3/AlN from capping layer were detected in capped- samples. For bare-ZrN samples, appearance of ZrO_2 and ZrO_xN_y up to sputter depth (d_{sput}) of 15 nm in depth-profile XPS data is in contradiction with measured $d_{ox} = 3.7$ nm, but explained from sputtering induced atomic inter-diffusion within analyzed sample. Appearance of artifacts in the XPS spectra from moderately sputtered ($d_{sput} = 0.2$ nm and 0.4 nm) capped-ZrN sample, provides an evidence to ion-bombardment induced modifications within analyzed sample.

1. Introduction

Thin film nitrides such as SiN, ZrN, GaN, AlN, AlGaN, etc., find applications in semiconductor electronics, optoelectronics, and MEMS based devices [1–5]. These applications require conformal nitride deposition over large area substrates with a strict tolerance on thickness uniformity. The self-limiting nature of material growth with atomic layer deposition (ALD) makes it the most suitable technique for nitride thin film deposition in critical applications [6]. Although many nitride ALD processes have been studied [7,8], x-ray photoelectron spectroscopy (XPS) characterization often shows a significant oxygen contamination in these ALD grown nitride films (as bound oxygen in the form of Ti—O/Ti—O—N bonds in TiN [9], Al—O/Al—O—N bonds in AlN [10], etc.). Moreover, depth-profile XPS studies have shown that this bound O is not localized to the surface but is distributed along sample thickness [9–12]. Several theories have been proposed to explain the observed O in nitride ALD films [13–15], yet this O-contamination issues has not been conclusively resolved. Considering application of ALD grown nitride thin films in emerging technologies, it is essential to identify potential mechanisms of O incorporation in ALD nitride films.

In this article we present a comparative XPS characterization of bare- and capped- zirconium nitride (ZrN) thin films deposited by plasma enhanced ALD (PEALD) as a case study to investigate whether post-growth ambient surface oxidation may explain the observed oxygen content in nitride ALD films. Our hypothesis is based on observation reported in [13,14], suggesting surface oxidation over post-growth ambient exposure as one of the factors that contributes towards the O-contamination in nitride ALD films. Furthermore, a comparative study of bare- and capped-ZrN PEALD samples allows for investigating ambient exposure effect alone, since O-contamination arising from other mechanisms (i.e. potential leaks in ALD reactor, process gas impurities, or any other process related factors) would be identical in both

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Abbreviations: PEALD, Plasma enhanced atomic layer deposition; ICP, Inductively coupled plasma; XPS, X-ray photoelectron spectroscopy; d_{Ox}, native oxide thickness on bare ZrN sample; t_{sput}, sputtering time in depth-profile XPS; d_{sput}, sputtered depth from the sample surface; d_{XPS}, effective XPS sampling depth from the surface.

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bare- and capped- ZrN samples deposited under identical process conditions. Room temperature oxidation at the surface of bare ZrN PEALD sample with ambient exposure is studied from spectroscopic ellipsometry (SE). XPS measurements on bare- and capped- ZrN samples before surface sputtering, or sputtering time (t_{sput}) = 0, is discussed considering presence of this native oxide layer at bare sample surface. Influence of ion-bombardment on redistribution of the original atomic concentration in the analyzed sample [16] is described. Considering such sputtering induced atomic intermixing effects, depth-profile XPS data measured (at sputtered depth (d_{sput}) = 1.5 nm, 4.5 nm, 9.0 nm and 15.0 nm) on the bare-ZrN sample is discussed. Sputtering induced artifacts are demonstrated from XPS measurements after moderate sputtering (effective d_{sput} = 0.2 nm, and 0.4 nm) of capped-ZrN sample.

2. Materials and methods

2.1. ZrN PEALD growth

ZrN PEALD depositions were carried in ALD-150LX (Kurt. J. Lesker) system under a continuous Ar (99.999% from Praxair) flow and total pressure ~1 Torr, and equipped with a remote- inductively coupled plasma (13.56 MHz ICP) source. Our ALD reactor is connected via a vacuum load lock (1×10^{-7} Torr base pressure) to a CMS-18 system (Kurt. J. Lesker) with a 3″ DC magnetron sputter gun (1×10^{-8} Torr base pressure). Reactor walls, ALD valves, and precursor delivery lines were maintained at 130 °C, 95 °C, and 110 °C respectively during deposition.

ZrN films were grown at substrate temperature of 150 °C using tetrakis-dimethylamino zirconium (TDMAZr) precursor and forming gas (5% H_2 + 95% N_2, from Praxair) reactant plasma (0.6 kW, ICP), with deposition cycle set to 0.10s TDMAZr precursor pulse, 12s post-precursor purge, 9s exposure to forming gas plasma, and 9s post-plasma purge, as reported in our earlier work [17]. For both bare- and capped- samples, ZrN deposition was performed under identical process conditions.

Bare ZrN samples for spectroscopic ellipsometry (SE) and XPS measurements were deposited on piranha cleaned p-type Si substrates (~2 cm × ~2 cm in dimensions). Whereas for the capped sample, Si substrates were coated with ~80 nm thick tungsten layer (by sputtering in CMS-18) and immediately transferred into ALD reactor under vacuum for ZrN PEALD deposition. The motivation for W coating on Si substrates prior to PEALD growth was to prevent O1s XPS signal emanating from either native silicon oxide layer from confounding our data.

2.2. Capping of ZrN PEALD sample

To minimize the impact of ambient exposure at room-temperature, we intended to apply a surface capping layer that restricts interaction of atmospheric moisture and oxygen with the underlying ZrN film, once these capped samples are transferred out of the ALD reactor. Based on the excellent moisture and oxygen permeation barrier characteristics [18], ALD grown Al_2O_3 film with trimethyl aluminum (TMA) and H_2O was selected to cap ZrN samples. Furthermore, to avoid oxidation of ZrN sample surface during H_2O exposure step of Al_2O_3 ALD, an intermediate layer of PEALD AlN (with TMA and forming gas plasma) was used between ZrN and Al_2O_3 as shown in Fig. 1.Furthermore, an additional advantage of selecting Al_2O_3 and AlN as capping layer is that the Zr3d and N1s photoelectrons have relatively longer inelastic mean free paths (IMFP's) in Al_2O_3 (λ_{Zr3d} = 2.94 nm; λ_{N1s} = 2.55 nm) and AlN (λ_{Zr3d} = 2.92 nm; λ_{N1s} = 2.54 nm) as compared to their IMFP's in ZrN native oxide layer (λ_{Zr3d} = 2.40 nm; λ_{N1s} = 2.09 nm). These IMFP values were obtained from NIST Electron Inelastic-Mean-Free-Path Database [19], and they suggest that inelastic scattering of Zr3d and N1s photoelectrons will be lower in Al_2O_3/AlN capping layer(s) than in the native oxide layer of equivalent thickness. Total thickness of the capping layers Al_2O_3 and AlN (each 1 nm) were selected such that they provide effective permeation barrier from atmospheric O_2/H_2O before XPS characterization, but simultaneously does not result in a total attenuation of the Zr3d and N1s emissions from underlying ZrN PEALD sample.

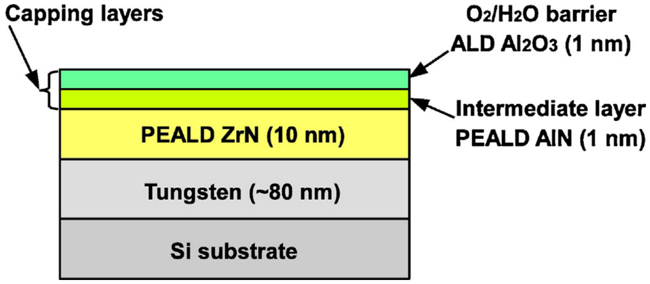

Fig. 1. Structure of capped ZrN PEALD sample illustrating O_2/H_2O barrier (1 nm ALD Al_2O_3) and intermediate layer (1 nm PEALD AlN) on the surface of 10 nm thick ZrN PEALD film grown on tungsten (~80 nm) coated Si substrate.

2.3. Spectroscopic ellipsometry (SE) data analysis

To study effect of ambient exposure on ZrN PEALD film at room temperature, SE measurements (M2000DI, spectral range: 0.73–6.4 eV, from J.A. Woollam) were made on bare ZrN sample at increasing duration of ambient exposure (t_{exp}). Thickness of the surface oxide (ZrO_x/ZrO_xN_y) layer and underlying ZrN PEALD film was determined from the analysis of measured SE data using CompleteEASE (ver. 4.48, J. A. Woollam) software.

In this analysis, the exposed ZrN film/substrate was modeled as a 4-layered stack consisting of a mixed surface oxide layer, underlying ZrN film, native SiO_2 layer and Si substrate. Parametric dielectric functions for ZrN and a mixed ZrO_x/ZrO_xN_y were represented by Drude-2 Lorentz [17] and Tauc-Lorentz [20] oscillators respectively.

2.4. XPS data analysis

XPS spectra was measured in a Kratos Axis Ultra spectrometer (at base pressure 1×10^{-10} Torr; Al K-α x-ray: 1486.29 eV, 4 keV Ar^+ for sputtering) and analyzed with CasaXPS (version 2.3.16). The background signal was subtracted using the Shirley function [21] and the component peaks represented with Gaussian-Lorentzian line-shape were fitted to the measured spectrum without data smoothening. Owing to spin-orbital splitting, Zr3d XPS emission consists of $Zr3d_{5/2}$ and $Zr3d_{3/2}$ peaks (binding energy difference of 2.43 eV, and intensity area ratio of 3:2). For visual clarity, pair of Zr3d emission peaks for every component in the measured Zr3d XPS spectrum are represented by a combined doublet features and only low energy $Zr3d_{5/2}$ peaks were labelled in Figs. 4–6.

In XPS analysis, the binding energy (BE) axis of the measured spectra was referenced with respect to the adventitious C1s peak assigned at BE of 284.6 eV. In literature, BE assignment to this adventitious C1s peak is seen to vary in the range of 284.6–285.6 eV [22]. Hence for unambiguous assignment of chemical states to the measured XPS emission features, a relative BE's denoted as Δ(#1, #2) = BE(#1)-BE(#2) was used and compared with the corresponding Δ from reported XPS studies. For example, to associate components Zr# and N# with Zr—N chemical bonds in ZrN, the Δ(N#, Zr#) in measured XPS data must be comparable to the reported Δ (=217.1 eV [23] for ZrN) from literature.