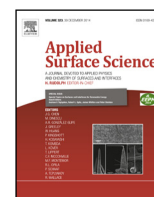
Applied Surface Science 328 (2015) 344–348

Contents lists available at ScienceDirect

Applied Surface Science

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



Probing initial-stages of ALD growth with dynamic in situ spectroscopic ellipsometry

Triratna Muneshwar*, Ken Cadien

Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta T6G 2V4, Canada

ARTICLE INFO

Article history:
Received 25 August 2014
Received in revised form 5 December 2014
Accepted 8 December 2014
Available online 15 December 2014

Keywords:
Dynamic in situ SE analysis
ALD film growth
Surface reactions
Bruggeman's EMA

ABSTRACT

The initial stages of ALD surface reactions are probed using dynamic in situ spectroscopic ellipsometry (d-iSE) technique during plasma-enhanced ALD of zirconium nitride (ZrN) thin films in spectral range of 0.73–6.4 eV. The measured change in the ellipsometry parameter Δ, with every precursor (TDMAZr) and reactant (forming gas plasma) exposure is interpreted as the combined effect of film growth and change in surface chemistry during ALD. We present application of Bruggeman's effective-medium approximation (B-EMA) in the analysis of d-iSE data to determine fractional surface coverage (θ) of ALD grown film at the end of every deposition cycle. During the deposition of first few ZrN monolayers, d-iSE datasets are analyzed on the basis of surface diffusion enhanced ALD growth, where the surface adsorbed precursor molecules can diffuse over substrate surface to occupy energetically favorable surface sites. The determined surface coverage of ZrN films highlights the effects of substrate enhanced ALD growth.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Modern semiconductor fabrication requires conformal deposition of extremely thin, pin-hole free films for high-k dielectric gate oxides for field-effect transistors and seed/diffusion barrier layers, for example. Moreover these films are also required to uniformly cover non-planar high-aspect ratio features like through-silicon vias, metal plugs etc., over large substrate areas (>700 cm^2). This substrate area may further increase to ~1500 cm^2 with the advent of 450 mm diameter Si wafers in high-volume device fabrication [1]. Atomic layer deposition (ALD) [2–5] is capable to meeting these stringent requirements. Since every ALD cycle consists of complementary surface reactions that are self-limiting in nature, film thickness can be controlled within a fraction of a nanometer with the number of deposition cycles. Also, in an optimized process, gas phase reactions are eliminated, hence ALD results in highly conformal, uniform and pin-hole free deposition over the entire substrate area.

Numerous ALD growth studies focusing on nucleation and surface reaction mechanisms have been reported in the literature [6–15]. Investigation into these ALD growth fundamentals is further fueled by the growing application of ALD in the fabrication of low-dimensional structures and devices [16,17]. Although in situ characterization techniques are crucial for ALD growth studies [7], very limited number of these could be applied to probe the actual deposition surface in real time.

Spectroscopic ellipsometry (SE) is a powerful optical technique used to simultaneously determine thickness and the dielectric function of thin films [18–21]. Earlier adsorption studies have shown that the ellipsometry parameters (Ψ, Δ) are sensitive to the surface coverage of adsorbed gases on clean surfaces [22–25]. Since SE does not interfere with the ALD process it is a compatible technique for in situ ALD study [26]. High-precision and faster acquisition rates for commercially available ellipsometers combined with appropriate ALD reactor design has enabled dynamic in situ spectroscopic ellipsometry (d-iSE) measurements on growing films in real-time. Although such dynamic measurements have been reported [27], in order to utilize d-iSE technique to its full potential requires careful interpretation and analysis of the measured data.

In this article we present the d-iSE data measured during plasma-enhanced ALD (PEALD) of ZrN thin films. The raw ellipsometry datasets are interpreted as a combined effect of film growth and changing surface chemistry during the ALD half-reactions. We have proposed an optical model consisting of Bruggeman's effective-medium approximation (B-EMA) to represent ALD growth in the partial surface monolayer coverage regime. In the early stages of ZrN deposition, the measured d-iSE spectra are analyzed on the basis of diffusive film growth, where the precursor

Abbreviations: ALD, atomic layer deposition; TDMAZr, tetrakis dimethylamido zirconium; PC$_R$SA, polarizer–compensator (rotating)-sample-analyzer; EMA, effective medium approximation.

* Corresponding author. Tel.: +1 780 729 6569; fax: +1 780 492 2881.
E-mail address: muneshwa@ualberta.ca (T. Muneshwar).

http://dx.doi.org/10.1016/j.apsusc.2014.12.044
0169-4332/© 2014 Elsevier B.V. All rights reserved.

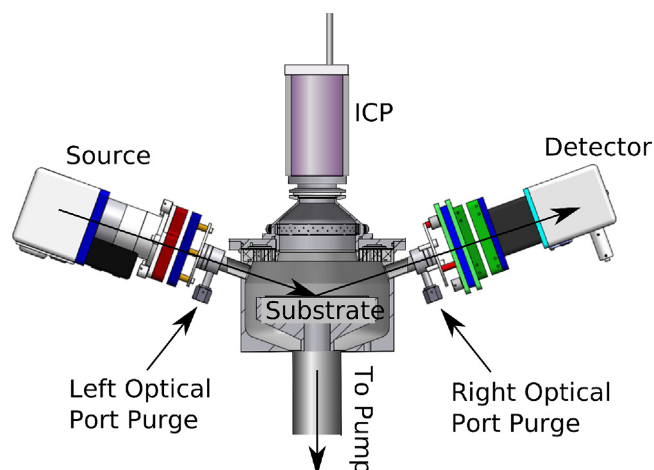


Fig. 1. Hardware configuration of ALD reactor and ellipsometer is schematically shown with Ar purging of the optical ports.

molecules can undergo surface diffusion to reach the energetically most favorable reaction sites.

2. Materials and methods

2.1. ZrN film deposition

Deposition was carried in a continuous flow ALD reactor (ALD150LX, Kurt J. Lesker) equipped with inductively coupled plasma (ICP) source shown schematically in Fig. 1. The system is also provided with optical ports for in situ characterization of ALD growth. Any parasitic depositions on these optical ports are prevented by continuous Ar purging during deposition.

ZrN PEALD films were deposited with tetrakis-dimethylamido-zirconium (TDMAZr) and forming gas (H_2:N_2) plasma (H^*, N^* and $NH_y{}^*$, where * denotes excited state) using cycle: 0.12 s TDMAZr/15 s Ar purge/15 s forming gas plasma (600 W)/15 s Ar purge, 150 °C substrate temperature. Zr precursor doses and plasma exposures were kept slightly longer than required for self-limiting growth to ensure that the ALD surface reactions attain saturation. Inert gas purges separating precursor and plasma steps were kept sufficiently long to allow complete removal of the reaction by-products and also to permit multiple d-iSE measurements. The substrate temperature for ZrN deposition was within the process temperature window for ALD. The optimization of ZrN PEALD process will be reported elsewhere.

ZrN films were deposited on the p-type Si (1 1 1) substrates measuring 15 mm × 20 mm, diced from 4-in. diameter wafers. These substrates were cleaned in Piranha solution, a mixture of concentrated H_2SO_4 and H_2O_2 solution 2:1 by volume, and securely stored in air-tight containers until deposition. The native oxide on the Si substrate surface was not removed since the surface –OH groups act as nucleation sites for the TDMAZr reaction [11].

2.2. In situ SE measurements

In situ SE measurements were taken on the growing film surface in the PC_RSA configuration [28] with the spectroscopic ellipsometer (M2000DI, J. A. Woollam). SE data were collected at a fixed angle of ∼70° from the substrate normal in the high-accuracy mode at +45° and −45° analyzer position to minimize errors induced by minor misalignment and imperfections within the instrument [29]. Since the surface chemistry changes continuously during precursor and plasma reactions at the substrate surface, it was essential to use short acquisition times for dynamic measurements.

SE measurements are represented as wavelength dependent amplitude ratio Ψ and phase angle Δ defined as, $\tan \psi_e^{i\Delta} = R^p/R^s$, where R^p and R^s are the complex reflection coefficients for *p*- and *s*-polarized light from multilayered samples. Using a model based analysis [28], thickness and dielectric function of the deposited material can be determined from the measured SE parameters (Ψ, Δ).

The d-iSE data reported in this article were averaged from multiple SE measurements collected over an acquisition time of 1.5 s (total of ∼3.0 s for two-zone measurement) to reduce signal noise within the acquired data. Analysis of SE parameters was performed using CompleteEASE software (version 4.48, J.A. Woollam) with built-in dielectric function models and extensive material library.

3. Theory

3.1. Bruggeman's EMA model for ALD films

Although the term ALD suggests a complete monolayer deposition per cycle, experimental results have shown that even for a "near-ideal" $AlMe_3/H_2O$ process, the steric hindrance from precursor molecules restricts deposition to a partial monolayer over an individual deposition cycle [5]. Theoretical models [11–13,15] developed for ALD considering partial-monolayer deposition per cycle are in good agreement with the experimental results.

In sub-monolayer gas adsorption studies [23,24] the surface monolayer with coverage θ was treated as a composite system consisting of the adsorbed species and voids (volume fractions θ and $1-\theta$ respectively) with dielectric function given by an effective-medium approximation [30]. It was shown that using such an effective dielectric function, the surface coverage of the partial monolayer could be reliably extracted from the analysis of the measured ellipsometry parameters. In this article, we propose the application of Bruggeman's EMA (B-EMA) [31,32] to model the dielectric function of the ALD grown partial monolayers shown schematically in Fig. 2.

In the B-EMA equation Eq. (1) ε_{ALD}, $\varepsilon_{\text{void}}$ and ε_θ are the dielectric constants for ALD film, void and the partial ALD film respectively, with θ and $(1-\theta)$ being the fractional surface coverage for ALD film and void, respectively. The screening parameter L $(0 \le L \le 1)$ depends on the geometrical shape and configuration of ALD clusters. Surface coverage of the ALD film is determined by treating θ as an additional fitting parameter in the analysis of SE data.

$$\theta \frac{\varepsilon_{\text{ALD}} - \varepsilon_\theta}{L\varepsilon_{\text{ALD}} + (1-L)\varepsilon_\theta} + (1-\theta)\frac{\varepsilon_{\text{void}} - \varepsilon_\theta}{L\varepsilon_{\text{void}} + (1-L)\varepsilon_\theta} = 0 \quad (1)$$

3.2. Surface diffusion enhanced mode of ALD growth

Depending upon the availability, distribution and selectivity of the surface reaction sites, ALD grown films are known to undergo (a) layer-by-layer deposition, (b) island deposition, or (c) random deposition mode of film growth. For evenly distributed reaction sites, the repulsive interaction between precursor molecules (steric factors) results in a uniform adsorption over substrate surface, leading to a layer-by-layer mode. A non-uniform or localized distribution of reaction sites leads to an island-growth [13]. In random deposition, negligible surface mobility is assumed for the adsorbed species such that they readily react at the surface without jumping into more stable neighboring sites [15]. However in a realistic case, at higher substrate temperatures, the adsorbed surface species would be sufficiently mobile to undergo surface diffusion and react at the energetically most favorable sites.

In the presence of ample reaction sites, a surface diffusion enhanced mode of ALD growth would be an intermediate between

Download English Version:

https://daneshyari.com/en/article/5348840

Download Persian Version:

https://daneshyari.com/article/5348840

Daneshyari.com