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Saturation profile measurement of atomic layer deposited film by X-ray microanalysis on lateral high-aspect-ratio structure



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ABSTRACT

Atomic layer deposition (ALD) of aluminum oxide thin films were applied on lateral high-aspect-ratio silicon test structures. The leading front of the film thickness profile is of interest, since it is related to deposition kinetics and provides information for ALD process development. A deposited profile was characterized using energy-dispersive electron probe X-ray microanalysis (ED-EPMA) and the results were analyzed using Monte Carlo simulation. A new procedure for obtaining relative film thickness profile from X-ray microanalysis data is described. From the obtained relative thickness profile, penetration depth of film at 50% of initial thickness and corresponding slope of thickness profile were determined at the saturation front. Comparison of the developed procedure was performed against independent measurements using optical reflectometry. ED-EPMA characterization of saturation profiles on lateral high-aspect-ratio test structures, supported by Monte Carlo simulation, is expected to prove useful tool for ALD process development.

1. Introduction

Atomic layer deposition (ALD) is a thin film deposition method based on alternating pulsing of gaseous precursors onto substrate surface and subsequent self-terminating gas-solid reactions [1–4]. One of the key factors for topical interest in ALD is its ability to grow conformal thin films on small-scale 3D structures. Such structures find application for instance in microelectronics, micro-electro-mechanical systems as well as porous catalyst supports [5–9].

Conformal films have the same thickness around 3D features [9]. However, accomplishment of conformality in ALD films is by no means self-evident. Non-conformal thickness profiles can arise from several reasons, when ALD process is not fully controlled by self-terminating surface reactions [10-12]. Especially in high-aspect-ratio structures, diffusion limited gas transport can result in non-conformal thickness profiles that depend on precursor doses.

Modelling of ALD process for high-aspect-ratio structures relates the leading front of the thin film thickness profile into processing conditions [13]. Consequently, quantification of ALD process performance can be contributed with straightforward thin film thickness profile measurement providing that appropriate test structures and methods are used. Many types of test structures have been proposed to study ALD process capabilities [9]. Recently, a new type of microscopic lateral high-aspectratio (LHAR) test structures has been developed [14–17]. An advantage

of the microscopic LHAR test structure is the possibility to remove the top membrane of it and analyze the deposited ALD film with conventional thin film measurement methods.

Basically, the measured film thickness profile in LHAR test structures is the saturation profile of the ALD process [17]. According to convention proposed in recent literature, two characteristic numbers can be extracted from saturation profiles: penetration depth of the film measured at 50% of the initial film thickness, expressed as $PD^{50\%}$, and slope of thickness profile at the $PD^{50\%}$ [13,16,17].

For post-growth measurement of thin film thickness, multitude of methods can be considered including energy-dispersive electron probe X-ray microanalysis (ED-EPMA). Thin film thickness measurement metrology has been discussed comprehensively within the framework of transistor gate oxide development [18,19]. The advantage of using ED-EPMA method is that high lateral resolution thickness profile data can be acquired from wide variety of film materials. In contrast, other X-ray film thickness measurement methods, such as X-ray reflectivity and X-ray fluorescence spectroscopy, lack sufficient lateral resolution for saturation profile measurements [20,21].

As ED-EPMA is primarily a chemical analysis method, the measured raw X-ray data provide spectral information and not film thickness values directly. To obtain film thicknesses from ED-EPMA x-ray data, several possibilities exist. Two type of general methods, the Monte Carlo (MC) simulation [22–24] and the film-modified approach based

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Fig. 1. Schematic illustration of the test structure: (a) uncoated test structure, (b) test structure after ALD coating and (c) test structure after suspended membrane has been removed allowing top-view examination of the deposited film (the illustration is not in scale and pillars that support the membrane are not shown; in reality L:H = 2000:1).

on depth distribution of X-ray generation (the function usually called $\phi(\rho z)$) [25–27], are currently in common use. Thin film software, based on the $\phi(\rho z)$ function, are also commercially available. In the case of a single layer films with known composition, various analysis procedures that are based on X-ray line intensity ratio techniques have been used in the past [28–30].

Regarding selection of the method to obtain film thicknesses from ED-EPMA raw data, the film-modified $\phi(\rho z)$ method is based on assumption of continuity of the $\phi(\rho z)$ function that is not always valid and prior knowledge of film density that is not necessarily available. Therefore, physically more generic MC approach can be beneficial especially in precisely definable applications as long as need for computational power will not become an obstacle.

Saturation profiles of ALD films haven't been quantified by any EPMA method previously in published literature. Conventionally, in film thickness calculations from spectral X-ray data film density needs to be known [31]. The purpose of this paper is to demonstrate the applicability of ED-EPMA for saturation profile measurement of ALD films in LHAR test structures without prior knowledge of film density values nor support of calibration with other experimental techniques. As for test material, aluminum oxide films were deposited using well-documented trimethylaluminum (Al(CH₃)₃, TMA)/water process [3,16,17]. Experimental EPMA results were analyzed using MC simulation. A new procedure for obtaining relative film thickness profile from ED-EPMA X-ray data is described that considers the film density issue and thereby enables the saturation profile measurement. Comparison of the results was performed against independent optical measurements.

2. Materials and methods

2.1. Specimen preparation

In the present work, micro-fabricated PillarHallTM LHAR chips of 3rd generation were used as a test structure. In the chip, rectangular lateral cavities of various sizes have been fabricated. A cavity has polysilicon membrane, supported by network of Si pillars, suspended above single crystal Si substrate. The dimensions of the structure used in this work had lateral cavity of 1000 μ m length with 500 nm high nominal gap between the polysilicon membrane and the Si substrate. The dimensions correspond to an aspect ratio (AR) of 2000:1 (hole equivalent aspect ratio (EAR) of 1000:1 [9]). An opening at the side of the cavity allowed diffusion of the ALD reactant gases in and out. In the test chip, two such cavities were positioned opposite to each other, leaving an initial open area between them without the polysilicon membrane. Fig. 1 shows a schematic picture of the structure. After deposition, the membrane was peeled off, allowing top-view examination of the deposited film. The 3rd generation PillarHallTM LHAR chip technology has been presented in ref. [17] in more detail.

Thin aluminum oxide films were deposited using TMA-water process in Picosun R-150 ALD reactor. The process temperature was 300°C and the pressure in the reactor was ca. 300 Pa. As the carrier and purge gas, nitrogen with a constant flow rate of 150 sccm was used. The TMApurge-water-purge sequence of 0.1-4.0-0.1-4.0 s was applied. The deposition for thickness profile measurement specimen was carried out with 1080 ALD cycles. Additionally, depositions with 810, 540, 270, and 160 ALD cycles were carried out for film thickness comparison. The specimens were named as A-E, respectively. The ALD cycle numbers were selected to give regular proportionality of 100/75/50/25 for the specimen A/B/C/D, respectively. In the case of specimen E, regular proportionality was not followed.

2.2. Experimental thin film characterization

Scanning electron microscopy (SEM) and ED-EPMA examination of specimens were carried out using Tescan Mira3 scanning electron microscope fitted with Thermo Scientific energy-dispersive X-ray spectrometer (EDS). The SEM was equipped with stable Schottky-type electron source. An accelerating voltage of 5 keV was used in the work. The low voltage was high enough to excite K-lines of all elements present in the specimens within a moderate interaction volume. No sample preparation for charging prevention was needed. In the examination, elemental X-ray mapping of the Specimen A surface was carried out first. Subsequently, EDS line scans of elemental profiles across the deposited film were measured. Outlier values due to pillars, holes exposed in pillar locations after membrane removal, and edges in surface structures were rejected from elemental profile data. The presented X-ray intensity profiles are averages of 10 scans in horizontal direction. Finally, EDS point measurements were performed for film thickness comparison.

For optical film thickness measurement, a FilmTek 2000M spectroscopic reflectometer was used. In the measurement, a $50 \times$ objective lens was applied, giving approximately 5 μ m spot size. For the line scan of the Specimen A, 100 data points were collected with 2 μ m interval. In the case of film thickness comparison specimens, presented results are averages of 35 measurement points.

2.3. Monte Carlo simulation of electron trajectories and characteristic X-ray emission

Characteristic X-ray emission is affected by composition, density and thickness of the film as well as properties of the substrate. Film density, ρ and thickness, *s* are non-separable variables in characteristic X-ray emission analysis combining to single mass thickness variable, ρs . To predict electron trajectories and emission of characteristic X-rays as a function of aluminum oxide film mass thicknesses on silicon substrate, MC simulations were performed. The simulation software DTSA-II was used in the calculations [32]. The electron trajectory computation used tabulated Mott elastic scattering cross sections and continuous stopping power model. In the computation of X-rays, also secondary fluorescence was covered. As far as composition of thin films are concerned, aluminum oxide was assumed to be stoichiometric Al_2O_3 based on previous studies of similar films with time-of-flight elastic recoil detection analysis (TOF-ERDA) [33]. Characteristic X-ray emission simulations were performed using 64 000 electron trajectories per sample.

2.4. Relative film thickness profile measurement procedure

Electron beam interaction with materials produces characteristic Xrays, whose intensity is determined in ED-EPMA measurement. Since ED-EPMA is essentially measuring amount of constituent elements in the film, the raw data was quantified to relative thickness by the following procedure. First, to exclude instrumental factors, experimental X-ray intensity values were normalized conventionally with pure element standards resulting k-ratios [34]. Next, MC simulation was used to predict k-ratio vs. mass thickness curve for current experimental setting.



Fig. 2. Secondary electron micrograph of surface of the specimen A with over layer of corresponding Al-K α X-ray net count map in red color.



Fig. 3. EDS elemental line profiles of Al, O and Si in the Specimen A that was deposited with 1080 ALD cycles.

The functional relationship obtained can be regarded as metrological measurement model [35]. Using the linear part of the simulated curve, calculated mass thickness values were found for each measured k-ratios. Finally, mass thickness values were normalized to relative thickness values by assuming uniform film density. Since constant density thereby cancels out, no prior knowledge of film density is required. In this way, relative film thickness profile was resolved point by point. The separate point measurements were linked to mass thicknesses in similar manner.

3. Results and discussion

3.1. Spatial distribution of X-ray emission

An elemental X-ray mapping of ALD deposited surface of Specimen A, after top membrane removal, is presented in Fig. 2. In the image, Al-Ka net count map is placed over secondary electron image. The elongated initial opening of the test structure is seen in the middle of the figure as a vertical area having 90 μ m width. The area is framed with residues of the removed polysilicon membrane. Points seen in the image are residues of the Si support pillars. The image shows overall spatial distribution of Al. Symmetrically from the initial opening, penetration of aluminum oxide in LHAR cavity areas are observed on both sides. It can be seen that aluminum oxide reaches more than 100 μ m into the cavity area. In extremely high AR features, the reactants typically do not reach the end of the cavity during deposition. This was also apparently the case in here.

In the Fig. 3 X-ray line intensity profiles of Al, O and Si from the Specimen A are presented. With the acceleration voltage of 5 kV the interaction volume of X-rays in the specimen exceeds the thickness of



Fig. 4. Monte Carlo electron trajectory simulation for 100 nm aluminum oxide thin film on Si substrate using 5 kV acceleration voltage.



Fig. 5. The k-ratios for Al as a function of number of ALD cycles.

the aluminum oxide film. Therefore, Si signal from the substrate was seen throughout the line scan. To exemplify the interaction volume, a Monte Carlo electron trajectory simulation for 100 nm aluminum oxide thin film on Si substrate using 5 kV acceleration voltage is displayed in Fig. 4. As function of distance, X-ray line intensities are changing in the Fig. 3. This reflects thickness profile of the film. At initial opening area, a constant film thickness was observed. At the beginning of the cavity, plateau continued, but with slightly increased film thickness comparing to the initial opening area. Finally, a knee point occurred at around 75 μ m from the beginning of the cavity, after which the thickness profile similar to what is observed for the TMA-water process also previously by optical reflectometry measurement [16,17].

3.2. Film thickness assessment

In the Fig. 5 measured k-ratios for Al-K α line from specimen A-E are plotted against numbers of ALD cycles showing linear dependency. In the case of TMA-water process, film thickness is reported to be nearly a linear function of number of ALD cycles [33]. Consequently, this indicates linear dependency also between measured k_{Al}-ratios and film thickness within the experimental conditions studied presently. Linearity of the data allows simple thickness scaling constant and zero thickness offset value to be assessed.

Characteristic X-ray emission of Al from aluminum oxide thin films in variable thicknesses and densities was modelled by MC simulation. In the Fig. 6, the MC simulated curve of mass thickness variable ρs against k_{Al} -ratio is presented. Nearly linear dependency between ρs and k_{Al} ratio were observed at the beginning of the curve to upper limit ρs value of around 35 $\mu g/cm^2$. This is in agreement with the Fig. 5 results. Depending on film density, the upper limit ρs value equals approximately to 100 nm film thickness. With higher k_{Al} -ratios the curve starts to bend upwards. This is due to conditions, where interaction volume of X-rays in the sample do not anymore exceed substantially the thickness of the aluminum oxide film. Eventually, interaction volume of X-rays does not reach the substrate at all and this condition equals to measurement of Table 1

Comparison of ED-EPMA and optically measured film thicknesses.

Specimen	Number of ALD cycles	k _{Al}	$\rho s (\mu g/cm^2)$	s (nm)	$s_{\rm OPT}$ (nm)
А	1080	0.331	30.9	100	103
В	810	0.250	23.5	76	78
С	540	0.162	15.5	50	54
D	270	0.074	7.4	24	30
E	160	0.041	4.4	14	20



Fig. 6. Monte Carlo simulated curve of mass thickness variable ρs versus k_{Al} -ratio for aluminum oxide thin films on Si substrate. Electron acceleration voltage in simulation was 5kV.



Fig. 7. Normalized thickness profile of aluminum oxide thin film in the Specimen A versus dimensionless distance \tilde{x} (\tilde{x} = measurement distance/cavity height). The slope of the profile has been fitted at PD^{50%} point.

bulk a luminum oxide instead of film. The lower limit ρs value equals approximately to 14 nm film thickness.

The working range (0.04< k_{Al} < 0.35) of nearly linear part of simulated data presented in the Fig. 6 was represented (R^2 = 0.9994) with Eq. (1).

$$\rho s = 91.4 \times k_{\rm Al} + 0.67 \tag{1}$$

Based on the Eq. (1), measured EDS elemental line profile, after kratio normalization, was transformed to mass thickness profile. Furthermore, with assumption of constant film density, mass thickness profile was transformed to relative thickness profile. This was performed by normalizing all mass depth values with the mass depth at the full film thickness. Relative thickness profile was achieved, because, obviously, the constant density cancels out (i.e. $\rho s/\rho s_{100\%} = s/s_{100\%}$). In Fig. 7, normalized film thickness profile of Specimen A is shown against dimensionless distance \tilde{x} . The dimensionless distance \tilde{x} was obtained by dividing measurement distance with the cavity height. The x-axis transformation was performed according to convention suggested in resent literature [17]. The zero point of the x-axis in Fig. 7 is located at starting point of the cavity in the test structure. The small thickness increase in the beginning of the curve is due to residues of the removed top membrane that were also seen in the Fig. 2.

From normalized thickness profile of deposited film, the $PD^{50\%}$ and the slope of the thickness profile at $PD^{50\%}$ were extracted. The $PD^{50\%}$



Fig. 8. Comparison of normalized thickness profile measurements between ED-EPMA and optical reflectometry in the Specimen A.

has been marked in Fig. 7 with a point and the corresponding reading was 195.2 with approximately 0.1% relative standard measurement uncertainty. The uncertainty estimate is based on electron trajectory simulation of Fig. 4. The slope of the thickness profile at $PD^{50\%}$ was -0.0108 with approximately 3% relative standard measurement uncertainty. The slope and uncertainty were estimated using linear least-square fitting of profile data around the $PD^{50\%}$ point. Similar numbers are reported previously for TMA-water ALD process in studies that used optical reflectometry for film thickness profile measurement [13,16,17].

3.3. Film thickness measurement comparison

In the Fig. 8 comparison of normalized thickness profile measurements between ED-EPMA and optical reflectometry is presented showing practically similar profiles near the $PD^{50\%}$ point. Spikes at the end of the optical reflectometry profile are due to residues of the Si support pillars that were in the path of the measurement line [17]. Non-zero thickness bias observed with optical reflectometry, close to the profile end, is shortly discussed together with the data in the Table 1.

Specimens A-E provide a reference material set for the ED-EPMA based film thickness determination procedure. Film thickness values from specimens A-E defined with ED-EPMA and optical reflectometry are compared in the Table 1. To begin with, measured k_{AI} -ratios and corresponding simulated mass thicknesses are presented in third and fourth columns of the Table 1, respectively. In conversion of mass thickness values to actual thickness values, film density needs to be known. With deposition conditions similar to this work, aluminum oxide thin film grown with ALD has been reported to have 3.10 g/cm³ density [33]. Using this value, ED-EPMA based film thicknesses are presented in the fifth column of the Table 1. In the last column of the Table 1, the independent optical film thickness measurement results are presented.

Electron probe X-ray microanalysis results agree with optical reflectometry results broadly. However, thicknesses obtained with electron probe X-ray microanalysis are systematically approximately 4 nm thinner than values obtained with optical reflectometry. This may be due to several factors. There can be inaccuracies in film density assumption. Moreover, there is presumable silicon dioxide interface layer in the structure that optical reflectometry is unable to distinguish. Furthermore, the Eq. (1) do not extrapolate exactly to zero and it has been reported that MC simulation systematically underestimate experimental k-ratios [36] Nevertheless, relative thicknesses measured with electron probe X-ray microanalysis are in $\pm 1\%$ mutual agreement when compared to relative numbers of ALD cycles and $\pm 2-5\%$ mutual agreement when compared to relative optical reflectometry thickness results. ED-EPMA method seems to perform better than optical reflectometry.

Amount of substance in film and film thickness are related by the density. ED-EPMA has clearly potential also for absolute film thickness measurement as far as method selectivity and sensitivity are concerned. However, traceable results would require mutual calibration approach with other measurement methods as presented in literature [37].

4. Conclusions

The paper shows that saturation profile of ALD films on LHAR test structures can be measured by ED-EPMA alone providing that film density is uniform throughout the profile. In consequence, penetration depth of film at 50% of initial thickness and corresponding slope of thickness can be determined at the saturation front. In the future, the ED-EPMA characterization approach of ALD film saturation profiles introduced in this work is expected to prove useful tool for process development. This applies especially in cases of films that are difficult to measure with optical methods commonly available.

Declaration of Competing Interest

R. L. P developed the concept of the microscopic LHAR conformality test and is the inventor of a related patent application.

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