Broas, Mikael; Liu, Xuwen; Ge, Yanling; Mattila, Toni Tuomas; Paulasto-Kröckel, Mervi

Galvanic corrosion of structural non-stoichiometric silicon nitride thin films and its implications on reliability of microelectromechanical devices

Published in:
Journal of Applied Physics

DOI:
10.1063/1.4923025

Published: 01/01/2015

Document Version
Publisher's PDF, also known as Version of record

Please cite the original version:
Galvanic corrosion of structural non-stoichiometric silicon nitride thin films and its implications on reliability of microelectromechanical devices

M. Broas, X. Liu, Y. Ge, T. T. Mattila, and M. Paulasto-Kröckel

Citation: Journal of Applied Physics 117, 245304 (2015); doi: 10.1063/1.4923025
View online: https://doi.org/10.1063/1.4923025
View Table of Contents: http://aip.scitation.org/toc/jap/117/24
Published by the American Institute of Physics

Articles you may be interested in

Structural and chemical analysis of annealed plasma-enhanced atomic layer deposition aluminum nitride films
Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films 34, 041506 (2016); 10.1116/1.4953029

Blistering mechanisms of atomic-layer-deposited AlN and Al₂O₃ films
Applied Physics Letters 111, 141606 (2017); 10.1063/1.4994974

LEARN MORE
Galvanic corrosion of structural non-stoichiometric silicon nitride thin films and its implications on reliability of microelectromechanical devices

M. Broas,1,a) X. Liu,2 Y. Ge,2 T. T. Mattila,1 and M. Paulasto-Kröckel1
1Department of Electrical Engineering and Automation, Aalto University, Espoo, P.O. Box 13500, FIN-00076 Aalto, Finland
2Department of Materials Science and Engineering, Aalto University, Espoo, P.O. Box 16200, FIN-00076 Aalto, Finland

(Received 27 March 2015; accepted 15 June 2015; published online 24 June 2015)

This paper describes a reliability assessment and failure analysis of a poly-Si/non-stoichiometric silicon nitride thin film composite structure. A set of poly-Si/SiNx thin film structures were exposed to a mixed flowing gas (MFG) environment, which simulates outdoor environments, for 90 days, and an elevated temperature and humidity (85 °C/95% R.H.) test for 140 days. The mechanical integrity of the thin films was observed to degrade during exposure to the chemically reactive atmospheres. The degree of degradation was analyzed with nanoindentation tests. Statistical analysis of the forces required to initiate a fracture in the thin films indicated degradation due to the exposure to the MFG environment in the SiNx part of the films. Scanning electron microscopy revealed a porous-like reaction layer on top of SiNx. The morphology of the reaction layer resembled that of galvanically corroded poly-Si. Transmission electron microscopy further clarified the microstructure of the reaction layer which had a complex multi-phase structure extending to depths of ~100 nm. Furthermore, the layer was oxidized two times deeper in a 90 days MFG-tested sample compared to an untested reference. The formation of the layer is proposed to be caused by galvanic corrosion of elemental silicon in non-stoichiometric silicon nitride during hydrofluoric acid etching. The degradation is proposed to be due uncontrolled oxidation of the films during the stress tests. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4923025]

I. INTRODUCTION

Silicon-based thin film structures are utilized in various Micro-Electro-Mechanical Systems (MEMS) devices. For example, devices relying on thin film structures include microphones, pressure meters, and spectrometers.1–3 Many thin film devices have to be sealed from the atmosphere to assure their normal operation.4 However, not all applications can be isolated from the ambient since their operation requires interaction with the atmosphere. The functional element of such devices is therefore exposed to airborne impurities and humidity, which can harm the normal operation of the device. For example, corrosion in electronics has been identified as a reliability concern even in indoor environments with critical airborne pollutant levels of less than 10 ppb.5

The prevailing choice of material in MEMS technology is silicon, which is generally considered reliable and inert material in normal atmospheric conditions at room temperature, although micron-scale poly and single crystal silicon are known to be susceptible to fracture failures under cyclic stresses.6,7 The fatigue-like failures have been proposed to be due to enhanced oxidation during cyclic loading together with simultaneous crack growth in the locally thickened oxide layer.8,9 However, also purely mechanical fatigue has been proposed to take place in micron-scale silicon.10 The stresses required to induce such fatigue-like failures (endurance limit) have been determined to be in the order of 1–2 GPa depending on the fabrication history and, thus, on the surface condition of the devices.11,12 For example, enhanced surface oxidation and coarse surface morphology have been observed in hydrofluoric (HF) acid release-etched polysilicon MEMS, where the structural polysilicon has been in contact with noble metallization, such as gold, during the release etching step.13 Nevertheless, silicon MEMS have been successfully demonstrated to operate also in more demanding environments such as in mass flow control systems for semiconductor gas and liquid distribution.14

Previously, we have reported a reliability assessment on poly-Si/SiNx thin film structures in which a mixed flowing gas (MFG) test, which simulates the effect of outdoor environments in an accelerated manner, was conducted for 90 days.15 To the knowledge of the authors, this was the first MFG test reported on silicon-based thin film structures. Brittle fractures were observed in the thin film membranes after sample handling despite no significant change had been detected in the electrical performance of the devices during the test period. This lead us to believe that membrane embrittlement had taken place during the exposure to the MFG chemicals. It was postulated that some type of mixture of environmentally-assisted oxide growth together with impurity segregation at grain boundaries would lead to the embrittlement process of the polysilicon part of the devices. However, the root cause was not identified. Therefore, the scope of this paper is to explore the observed embrittlement phenomenon further. Enhanced oxidation due to cyclic loading and associated fatigue failures, and purely mechanical
fatigue as hypotheses for the root cause of failures are dismissed since the stress levels would never exceed magnitudes of 1–2 GPa during the MFG test or sample handling.

The MFG test was repeated in this study and analysis on the silicon-based thin film structures was conducted with various characterization techniques. First, the degree of degradation in the mechanical performance of the thin films was characterized by utilizing nanoindentation where the forces required to fracture thin films were compared between treated and untreated samples. Thereafter, structural and chemical analyses were conducted utilizing optical, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Furthermore, chemical analysis was conducted utilizing X-ray photoelectron spectroscopy (XPS) depth profiling with argon sputtering.

II. MATERIALS AND METHODS

A. Thin film structure under study

The thin film structure used in this study was based on a parallel capacitor membrane design. The capacitor electrodes comprise of two conducting polycrystalline silicon thin film membranes which are separated by a 5 μm air gap. The top membrane is fixed, whereas the bottom membrane is supported only by a single cantilever beam and is thus a free floating type membrane. The membranes are fabricated using surface micromachining techniques. Health monitoring of the structures during the exposure to the harsh environments is conducted by measuring the capacitance between the membranes. The change in the separation distance between the membranes is detected by the change in the electric capacitance between the membranes. Consequently, the capacitive response of the device to background noise will depend on the material properties of the thin films. Figure 1 presents an overview of the structure. The top membrane is perforated so that an etchant can penetrate under the top membrane in order to free it. In the release etching process HF attacks a sacrificial silicon dioxide layer that has been deposited between the membranes. The thickness of the oxide layer controls the distance between the electrode membranes. The top membrane consists of two layers—a conducting polysilicon film and an insulating non-stoichiometric silicon nitride (SiNx) film. The nitride film is approximately 940 nm in thickness and the polysilicon film has the thickness of approximately 460 nm. Composite structures can be utilized, for example, to tailor the stress state of the structure. The polysilicon had a columnar microstructure with grains expanding the whole thickness of the thin film. Average grain diameter was approximated from SEM and scanning TEM (STEM) micrographs to be in the order of 200–400 nm (Fig. 1). The SiNx had an amorphous microstructure.

B. Experimental setup

The thin film structures were exposed to a mixture of flowing gases for 90 days in an environmental test chamber system (Weiss WK11 600/40) to simulate the outdoor use conditions of modern MEMS devices. The mass flows of the impurity gases were measured from inlet valves and the temperature and humidity with a sensor (Vaisala HMT 333) located inside the chamber. The concentrations of the gases inside the chamber were calculated according to measurements from the inlet valves and air turnover rate of the chamber. According to the measurements and the calculations, test environment was the following: temperature 30°C, humidity 70% R.H., Cl₂ concentration 55 ppb, H₂S concentration 350 ppb, NO₂ concentration 350 ppb, SO₂ concentration 350 ppb, and air turnover rate 8 times/h. A more detailed description of the test is included in Ref. [17]. Furthermore, thin film structures were also exposed to an elevated temperature and humidity (85°C, 95% R.H.) test for 140 days to compare the effects of only elevated temperature and humidity on the mechanical performance of the thin film structures. Elevated temperature and humidity testing of Si-based thin films are relevant since such environments can induce oxidation of Si, fatigue-like behavior of Si, and anodic oxidation of Si with the help of bias voltages. Though usually deliberate oxidation of Si takes place in the range of hundreds of degrees of Celsius. Rather long times in both of the tests were chosen to drive any occurring reactions to their completion. Both of the tests were still considered to be realistic in a sense that failure mechanisms would not be expected to be altered drastically compared to normal use conditions.

Nanoindentation measurements were conducted to the thin film membranes employing a nanomechanical instrument (Hysitron TriboIndenter). Nanoindentation was employed to induce a fracture in the top membranes and record the force upon fracture initiation. Five different pre-treatments and untreated reference samples were measured and their respective fracture forces were then compared. The five pretreatments were 140 days in 85°C and 95% R.H., 50 days in the MFG test (both electrically biased and unbiased...
devices), and 90 days in the MFG test (both electrically biased and unbiased devices). To investigate whether degradation took place in SiNx or poly-Si two different locations on the top membrane were indented. One location was completely SiNx, whereas the other had both SiNx and poly-Si layers (Fig. 2). Sample sizes were from 4 to 6 with a total of 61 samples. A cube corner tip was used in the pure SiNx site and a Berkovich tip in the SiNx + poly-Si composite site. The cube corner tip had a three-sided pyramidal shape with 90° total include angle and a 40 nm nominal radius of curvature. The Berkovich tip had a nominal tip radius of 130 nm. The sharper cube corner tip was selected for the SiNx site in order to achieve fracture initiation with minimum displacement by having the maximum stresses immediately under the tip. The Berkovich tip has a wider nominal tip radius than the cube corner tip. Therefore, the stress distribution was thought to be more uniform in the composite structure (i.e., SiNx + poly-Si) with maximum stresses concentrated on the material surfaces due to tensile/compressive stresses. A more detailed stress analysis of the indentation process with the help of finite element method is presented in Ref. 17.

A TEM lamella of a stress tested sample was prepared with a focused ion beam (FEI Helios NanoLab 600 FIB) system using a lift-out technique.20 Shortly summarizing, first a thin layer of protective Cr was sputtered on top the sample to protect it from Ga⁺ ion-milling induced damage.21 Ga is used as the ion source in the ion-column of the FIB. A thicker protective Pt film was further deposited using ion-assisted deposition of the FIB tool. Second, a thin cross-section was milled from the top membrane. The cross-section included both SiNx and poly-Si material layers. The cross-section was welded to a nanomanipulator tip using the Pt ion-assisted deposition, released from the top membrane utilizing ion milling, and moved to a TEM grid. Finally, the cross-section was thinned and polished using ion milling to make it suitable for TEM imaging. The TEM sample was then imaged at 200 kV with an analytical transmission electron microscope (FEI Tecnai F20-FEGTEM S-Twin) equipped with a Gatan Multiscan charge-coupled device camera.

III. RESULTS
A. Nanoindentation

The measured nanoindentation data was normalized with respect to the average fracture force of the untreated samples for both indentation sites separately. The extracted data was in thousands of micronewtons. The fracture force in Newton does not present actual fracture strength, since the actual stress, due to applied force on the material, is a function of the geometry and material properties. Therefore, the data is presented in a normalized format to describe the proportional strength of the devices. The normalized results are presented in Figures 3 and 4 for the bare SiNx and SiNx + poly-Si indentation sites, respectively. Notable differences between sample treatments are visible for the bare SiNx site where degradation of the SiNx part of the membrane seems to occur due to different treatments. The SiNx + poly-Si site, by contrast, was more tolerant towards the different treatments. The fracture strength of chemical vapor deposition silicon nitride is 4–5 times higher than that of poly-Si.22 Therefore, it is probable that the fractures in the SiNx + poly-Si site initiated on poly-Si assuming the fracture strength of degraded SiNx would still be higher than in poly-Si. Furthermore, this would mean that poly-Si did not undergo degradation during the stress tests.

Abbreviations used in the charts are untreated reference (REF), 140 days 85°C 95% R.H. (RH), MFG test 50 days biased (MFG50), MFG test 50 days unbiased (MFG50UB), MFG 90 days biased (MFG90), and MFG test 90 days unbiased (MFG90UB). The sample sizes were six for SiNx REF and SiNx RH and four for SiNx + poly-Si MFG50, whereas the sample sizes were five for the rest of the SiNx and the SiNx + poly-Si samples (total 61 samples). Several statistical tests were then employed to analyze the trends visible in the normalized graphs between different treatments and the untreated samples. First, Shapiro-Wilk test for normality was used on all of the groups. Most of the groups had p-values indicating normal distributions (p-values > 10%).

FIG. 2. Micrographs displaying the nanoindentation sites on the top membrane.

FIG. 3. Nanoindentation data normalized with respect to the reference untreated samples collected from the bare SiNx site. Error bars represent ± one standard deviation (± 1σ).
which is a prerequisite for analysis of variance (AOV). The only group with a p-value lower than 10% was SiNx + poly-Si RH but was still included in the AOV. One-way AOV was then employed to calculate the p-value for between-groups effect, i.e., to see whether there is statistically significant difference in the means of the groups. High p-values of 0.35 for the SiNx site and 0.47 for the SiNx + poly-Si site yielded insignificant changes in the mean fracture forces between treatments and reference samples. However, the test assumes that the variances are the same for all of the groups. Based on Fig. 3, this is not the case between the reference samples and the treated samples for the bare SiNx site. The homogeneity of variances was tested simultaneously with the one-way AOV which indeed yielded a low p-value of 0.023 in the SiNx site with the Levene’s test (0.54 in the SiNx + poly-Si site). That is, the variances for SiNx samples were different with statistical significance. Two sample T test was then used to compare the p-values for the means and the variances for all pair-wise combinations of the SiNx samples. These results are presented in Table I.

There is little statistical evidence that the means of the fracture forces would change between the treatments and references. However, the difference in the variances between the untreated reference samples and groups MFG50, MFG90UB, and MFG90 are statistically significant on a risk level of <10%, i.e., the variance in the fracture force of SiNx changes due to these treatments. This can be interpreted as the material initially having a population comprising of weak and strong samples. The MFG testing then affects mainly the strong population bringing their fracture force down simultaneously decreasing the variance. The elevated temperature and humidity test does not seem to induce the same affect with statistical significance. Furthermore, there is no statistical difference in the fracture force means or variances as a function of time or electrical biasing in the MFG test. The degradative mechanism operating in the MFG environment has therefore likely been driven to its completion in 50 days of testing.

### B. Fractography

The fracture surfaces of the indented samples were analyzed with visible light and electron microscopy (Jeol JSM-633OF field emission SEM). All of the indented samples

![Normalized fracture force vs. sample treatment](image)

**TABLE I.** Tabulated two sample T test p-values for the means and folded F test p-values for the variances between different treatments. Pooled variance calculation was used when F test for variance had a p-value higher than 10%.

<table>
<thead>
<tr>
<th>Site</th>
<th>REF vs. MFG50</th>
<th>REF vs. MFG90</th>
<th>REF vs. MFG90UB</th>
<th>RH vs. MFG50</th>
<th>RH vs. MFG90</th>
<th>RH vs. MFG90UB</th>
<th>MFG50UB vs. MFG50</th>
<th>MFG50UB vs. MFG90</th>
<th>MFG50 vs. MFG90UB</th>
<th>MFG50 vs. MFG90</th>
</tr>
</thead>
<tbody>
<tr>
<td>REF</td>
<td>0.1738</td>
<td>0.0104</td>
<td>0.0894</td>
<td>0.1738</td>
<td>0.1145</td>
<td>0.2546</td>
<td>0.3716</td>
<td>0.3716</td>
<td>0.3716</td>
<td>0.3716</td>
</tr>
<tr>
<td>MFG50</td>
<td>0.1014</td>
<td>0.0388</td>
<td>0.0388</td>
<td>0.1014</td>
<td>0.0947</td>
<td>0.0947</td>
<td>0.1738</td>
<td>0.1738</td>
<td>0.1738</td>
<td>0.1738</td>
</tr>
<tr>
<td>MFG90</td>
<td>0.0894</td>
<td>0.0388</td>
<td>0.0388</td>
<td>0.0894</td>
<td>0.0947</td>
<td>0.0947</td>
<td>0.1014</td>
<td>0.1014</td>
<td>0.1014</td>
<td>0.1014</td>
</tr>
<tr>
<td>MFG90UB</td>
<td>0.1145</td>
<td>0.0947</td>
<td>0.0947</td>
<td>0.1145</td>
<td>0.0947</td>
<td>0.0947</td>
<td>0.2546</td>
<td>0.2546</td>
<td>0.2546</td>
<td>0.2546</td>
</tr>
</tbody>
</table>
were imaged with visible light microscopy and selected samples were imaged with the SEM. Figures 5 and 6 present typical fracture surfaces of both of the indentation sites as imaged with a visible light microscope which was used as the alignment microscope in the nanoindentation system. No clear differences were seen in the fracture paths between different treatments for the same indentation sites.

Some of the fracture surfaces were characterized with the SEM. Figure 7 presents these observations in the SiNx indentation site. No clear differences were visible between

FIG. 5. Micrographs of SiNx sites post indentation. Reticles indicate the site of the indentation. (a) Untreated reference. (b) MFG test 90 days biased.

FIG. 6. Micrographs of SiNx – poly-Si sites post indentation. (a) Untreated reference. (b) MFG test 90 days unbiased.

FIG. 7. SEM micrographs of SiNx sites post indentation. The micrographs are from fracture surfaces at the nanoindentation site displayed in the center micrograph. All of the samples display a reaction layer on top of SiNx. (a) Untreated reference (tilted view), (b) 140 days 85°C, 90% R.H (tilted view), (c) MFG test 90 days biased (top view), and (d) MFG test 50 days biased (tilted view).
different treatments in either of the indentation sites. However, a reaction layer was observed on top of the SiNx in all of the samples including the untreated references. Therefore, the layer had to form either during sample preparation or during the fabrication process. The sample preparation included only removal of a protective lid by heating and removing the lid with tweezers. No chemical processes were involved in the lid removal. Therefore, the most likely explanation for the formation of such a reaction layer is a reaction that has occurred during the thin film structure fabrication. Thickness of the film was evaluated to be in the order of 100 nm.

C. Microstructure and chemical composition analysis

A TEM sample was prepared from a 90 days MFG-tested sample to study the reaction layer further and to look for any other anomalies in the microstructure due to the MFG test in the top membrane of the thin film structure. Figure 8 presents TEM micrographs from the top and bottom sides of the top membrane in the SiNx + poly-Si site.

Starting from the top of the TEM micrographs, ion-milling-related debris consisting of Pt, C, and Ga was discovered on top of the reaction layer previously noted from the SEM micrographs. Underneath the debris-layer, the protective Pt/Cr layer was detected. These findings were further confirmed with the energy dispersive X-ray spectrometer (EDX) that was equipped with the TEM. The Pt/Cr film was partly discontinuous; hence ion bombardment-induced damage has likely taken place on the sample in these areas. Furthermore, the previously discovered reaction layer was visible on top of the non-stoichiometric silicon nitride. Four phases were visible in the film where the bottommost phase resembled a thick oxide layer sometimes found on top of bare silicon samples due to enhanced oxidation. The thickness of the whole film was approximately 107 nm. The diffraction pattern was obtained with the smallest available aperture which covered some of the protective layer besides the reaction layer. The pattern indicated a mainly amorphous structure. The few distinct diffraction spots matched a face-centered cubic structure with plane distances matching those of Pt. This is consistent with the protective Pt deposited with the FIB. Furthermore, high resolution TEM (HRTEM) images of the reaction layer showed an amorphous structure though a few groups of lattice planes were found in the phase on top of the bottommost phase corresponding to grain sizes of a few nm. The poly-Si side of the sample did not display any irregularities.

XPS measurements with combined Ar sputtering for depth profiling were conducted in order to analyze the chemical composition of the reaction layer and to detect any impurities in the SiNx part of the top membrane. The XPS measurements were conducted to an untreated reference sample and a 90-day MFG-tested sample (Fig. 9). Both of the samples had trace amounts of fluorine (F), carbon (C),
and tin (Sn) on top of the membranes (depth in the range of few nanometers). The fluorine and carbon are likely related to a fluoropolymer, such as the passivation polymer used in deep reactive ion etching (DRIE). The trace amounts of tin may originate from the reflow process of tin-based solders. The sputtering was ended either when or just before the poly-Si layer was reached as there was no indication of degradation in poly-Si according to the analysis of the fracture forces and fractography. The material removal rate was approximately 65 nm/min assuming a 940 nm SiNx layer and by noting that the poly-Si was reached in 14.5 min of sputtering. According to the depth-profiling, the amount of oxygen drops rapidly in the untreated sample at the depth of ~75 nm reaching 4 at.%, whereas in the 90 days MFG-tested sample the amount of oxygen drops gradually reaching 4 at.% at the depth of ~150 nm. Figure 10 illustrates these findings. Furthermore, the XPS spectrum also revealed that the atomic proportions of silicon and nitrogen were approximately 3:2 in the SiNx, i.e., the film was silicon-enriched silicon nitride (Si3N4). Figure 11 presents spectroscopic XPS data displaying distinct peaks of silicon bound in Si3N4 and pure Si. The spectrum was not calibrated according to any known elements. However, if the spectrum is correct with setting elemental Si 2p peak to 99.5 eV, the Si3N4 peak will be located at 101.6 eV which is in reasonable agreement with the literature. The analysis spatial spot size was in the order of 100 μm, whereas the membrane analyzed had a diameter of 600 μm. Therefore, the effects of surrounding silicon substrate cannot be completely excluded. It is noteworthy though that the stoichiometry of chemical vapor deposition silicon nitrides is dependent on the process parameters and different compositions with varying ratios of Si, N, and H can be achieved.

IV. DISCUSSION

The three main findings presented above were (i) the discovery of a reaction layer on non-stoichiometric silicon nitride, (ii) oxidation to depths of 100 nm range in the reaction layer, and (iii) the degradative influence of the stress tests to the SiNx in the thin film structure. First, a possible root cause is presented for the formation of the reaction layer derived from the theories of formation of porous-Si and galvanic corrosion of poly-Si. Second, the oxidation behavior is discussed based on the explanation for the reaction layer formation. Finally, the degradative influence of the stress tests is considered.

Poly-Si is known to undergo galvanic corrosion when subjected to diluted HF and other HF-based chemistries when in electrical contact to noble metals such as Au. Such galvanically corroded poly-Si has similar morphology to porous silicon and the chemical reaction taking place has been suggested to be the same as for the formation of porous-Si. In the chemical models of the formation of porous silicon holes need to be injected to the valence band of silicon at the silicon-electrolyte interface in order to form porous-Si. This implies that porous silicon formation can take place if p-type silicon is used or if n-type silicon is irradiated to generate hole-electron pairs at the silicon-electrolyte interface. Furthermore, porous-Si is formed only under a certain threshold electrical driving potential, i.e., the potential of the Si electrode needs be in a certain positive regime with respect to a standard counter electrode in order to drive holes to the Si-electrolyte interface. In this regime silicon is directly etched forming porous-Si. If the electrode driving potential for the reaction is large enough, electropolishing will take place. In electropolishing, rather than silicon being etched, the silicon surface oxidizes and is subsequently etched by the HF thus resulting in uniform erosion of the surface.

The transition voltage between the two regimes is determined by the electrolyte concentration (i.e., HF concentration), temperature, and relative electrode areas. In the porous-Si formation regime, the supply of holes to the surface of Si is the reaction limiting factor, whereas in the electropolishing regime supply of fluoride species limits the rate of the oxide etching. Both of these reactions have been speculated to take place in the unintended galvanic cell which can form between Si and Au in HF-based electrolytes. However, the exact mechanism of galvanic corrosion of Si during HF etching is not completely understood. Furthermore, there is also various reports of galvanic...
corrosion taking place in n-type silicon during wet HF etching regardless of not being directly irradiated by light. However, some background illumination may have been present while HF-based chemistry submerge of the devices have taken place. Intrinsic, non-doped, silicon has also been shown to be susceptible to galvanic corrosion. Therefore, we propose that in silicon-enriched nitride galvanic corrosion of silicon can take place too. Considering that the top membrane was connected to gold bonding pads and that release etching step utilizes HF-based chemistries a galvanic cell can have formed between the membrane and the bond pads. Consequently, the silicon-enriched nitride has contained enough “free” silicon for the galvanic corrosion to take place in an observable manner. Indeed, XPS data revealed elemental silicon in the bulk of the nitride film. Furthermore, the SEM observations show similar surface morphology as reported previously on galvanically corroded poly-Si. Since the top surface of the membrane has been in prolonged exposure to HF during the release step it is also expected that the corrosion has progressed further as compared to the bottom surface of the membrane. Therefore, no corroded morphology was detected in the bottom surface of the membrane.

A thick oxide on Si surface can either form because a porous-like, galvanically corroded silicon surface oxidizes rapidly in normal atmospheric conditions due to the high surface area, or because the silicon has undergone electropolishing. The thickness of the native oxide of bulk silicon in room temperature is in the order of a couple nanometers and on pristine silicon nitride the native oxide is even thinner, in the order of a nanometer. Oxidation of crystalline silicon nitride is very slow in higher temperatures too; over 1200°C in an 1 atm dry O2 atmosphere is required to induce reasonable oxide growth (>50 nm SiO2 in 6 h). Regardless, rapid oxidation of silicon nitride has also been reported for plasma-enhanced chemical vapor silicon nitride deposited in low temperature (in the order of 100°C). The authors proposed the rapid oxidation to be due to a porous nature of the low temperature-deposited films but did not present any structural evidence to support the claims for porosity. The thicknesses of the oxidized layers detected in this study were orders of magnitude thicker compared to the typical native oxides of silicon and silicon nitride. The relatively thick oxides of the membranes, measured by the XPS, are thus explained through the galvanic corrosion of the silicon-enriched nitride either due to electropolishing or porous-Si formation mechanism. Especially, in the case of porous-Si formation, the surface area of corroded SiNₓ could be considerably large and the remaining free silicon could react rapidly with oxygen. Furthermore, as discussed above, also silicon nitride can form a thin oxide in room temperature. As pointed by the TEM images, the films are highly non-uniform which implies that the galvanic reaction has been at least partly on the porous reaction side. Therefore, the measured oxide depth-profiles are proposed to be mainly due to the oxidation of the porous layer regardless whether the exposed material has been elemental silicon or silicon nitride.

The 90 days MFG-tested sample has likely oxidized deeper compared to the untreated reference (as pointed out by the XPS data) partly due to the elevated temperature and humidity in the test chamber. As for the role of the impurities in the MFG test, chemical analysis did not point out towards any impurity segregations inside SiNₓ nor the porous-like reaction layer. However, the role of oxidizing compounds in the MFG chamber, such as NO₂ and SO₂, is not clear. The statistical analysis pointed out that the MFG environment indeed affected the fracture properties of the SiNₓ. Therefore, some type of interaction is expected between either the reaction layer or the SiNₓ and the MFG gases. Porous silicon can be utilized in gas sensing applications for a variety of gaseous compounds, including NOₓ, SO₂, and H₂S. There is also evidence of irreversible interaction between porous silicon and NO₂. It is therefore reasonable to believe that the gases could have affected the oxidation behavior or induced other type of material degradation of the porous-like reaction layer. The thicker surface oxide in the MFG-tested sample could consequently lead to impaired fracture properties of the material. For example, the fracture strength of silicon dioxide is in the order of 1 GPa for poly-Si it is in the order of 2–3 GPa (values close to 1 GPa have been also reported), and for Si₃N₄ > 10 GPa though ultimately the fracture strength of brittle materials depends on the initial flaw size. Finally, oxidized surfaces can also create increased stresses inside the material due to volumetric expansion of the oxidized compound.

V. CONCLUSIONS

Two accelerated stress tests, a MFG test and an elevated temperature and humidity test were conducted on a poly-Si/ non-stoichiometric silicon nitride thin film composite structure. The effect of the stress tests on the mechanical strength of the films was measured by fracturing treated and untreated thin films with a nanoindentator. Statistical analysis of the nanoindentation data revealed degradation of the structure during the MFG test. Further inspection revealed a porous reaction layer on the top membrane of the thin film structure. The reaction layer had formed on silicon-enriched nitride during device fabrication since also untreated samples contained the layer. The morphology of the film resembled that of widely reported galvanically corroded poly-Si. Galvanic corrosion of polysilicon can take place during HF release etching when the silicon structures are in contact with noble metals such as Au. In this study, the structure also had gold bonding pads for electrical measurements, which were in contact with the nitride, and the structure had been fabricated employing typical micromachining techniques. The chemical reaction for the galvanic corrosion of Si has been linked to porous-Si formation mechanisms. This implies that it is very unlikely that stoichiometric silicon nitride would corrode with the same mechanism as poly-Si or at all. However, since the nitride was silicon-rich the corrosion damage of the structure is explained by the anodic reaction of the elemental silicon. Galvanic corrosion of silicon-enriched nitride thin films is a novel finding. Furthermore, the applied MFG test oxidized (4 at. % oxygen) the corroded nitride to a depth of
~150 nm in contrast with oxidation depth of ~75 nm in an untreated reference sample. The uncontrolled oxidation of reactive porous surfaces then affected the mechanical strength of the films which depicted large scatter before stress testing and degradation after testing in forces required to fracture the films.

ACKNOWLEDGMENTS

The authors would like to thank Antti Peltonen for helping with the FIB sample preparation at Micronova, the Centre for Micro and Nanotechnology (Aalto University). Jyrki Juhanoja is thanked for the XPS analysis at Top Analytica Ltd.