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Advanced Process Equipment for PECVD Silicon Nitride Deposition – an Experimental Study

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Originally developed Plasma Enhanced Chemical Vapor Deposition (PECVD) device is explored to produce the silicon nitride films to be used as a material for surface micromachined capacitive ultrasound transducers. Silicon nitride is deposited from silane and ammonia gas mixture diluted in argon in the 13.56 MHz RF plasma with adjustable power. The conditions of deposition experiments were modified alternating the silane to ammonia flow ratio and the RF power, while other process parameters were supposed to be constant. The process responses measured were the deposition rate, film thickness, refractive index, surface morphology and film composition. It was found a strong influence of silane to ammonia flow ratio to the deposition rate, the refractive index and the composition of the film. Greater ratios, causing higher deposition rates, tend to give the lower refractive index, poorer surface and lower nitrogen content in resulting film. The RF power was also found to non-linearly influence the deposition rate and resulting film properties. Although the performance of the new apparatus was found to be reliable enough, the X-ray photoelectron spectrometry discovered elevated oxygen content, which is to be reduced by reducing the quantity of residual gases in deposition chamber.
Keywords: PECVD silicon nitride, RF plasma deposition equipment, cMUT manufacturing.

INTRODUCTION

Synthesis of silicon nitride thin films is the key issue in semiconductor industry. It is traditionally used as a passivation, moisture proofing and mechanical protective layer for integrated circuits [1, 2], as a mask layer for selective oxidation and dry etching [1, 3], as one of the dielectric materials [4], especially in a stacked layers of DRAM capacitors [5] and in similar applications, where combination of perfect electrical insulation, chemical passivity and mechanical fastness is essential.

Following the recession of the microelectronics industry at the end of past century, a turnout of new technologies, which can be summarized as the technologies of microscopic systems (microsystemotechnics), is the fact we face today. Considerable part of the technological knowledge, accumulated in the context of microelectronics, today is transferred to produce various electromechanical, optical and chemical components, which, being at the sizes of few micrometers, are integrated on-chip with the driving electronics. Here silicon nitride comes to serve as a foundation for surface micromachined components, being the main constructive material for microscopic electromechanical systems (MEMS) [6, 11 – 15].

The Low Pressure Chemical Vapor Deposition (LPCVD) technique is related with the economical and technological drawbacks [1 – 4]. Since the LPCVD nitride has to be deposited from silane (monosilane SiH_4 or diclorsilane SiH_3Cl_2 are of most common use) and ammonia (NH_3) at very high temperature (over 800 °C) at prolonged process time, many issues can arise including excessive solid state diffusion, junction leakage and metal silicide agglomeration [1, 2]. The Plasma Enhanced Chemical Vapor Deposition (PECVD) silicon nitride process is usually chosen either to reduce the thermal budgets or to avoid undesirable thermal effects [1, 3, 17], or to be able to adjust the properties of resulting film more flexibly [5, 9, 10]. In many cases diverse mixtures of silane with ammonia, diluted in nitrogen, are used for deposition in 13.56 MHz RF plasma.

Essential parameters of the films for the membranes of the surface micromachined capacitive ultrasound transducers (cMUT) are the film thickness, good integrity and surface smoothness, good step coverage, selectivity to the wet etching of the sacrificial layer, mechanical strength and intrinsic stress. As reported in previous studies of PECVD silicon nitride deposition [2, 3, 5, 7, 9], many of these parameters are controversial to the common process parameters, such as plasma energetic density, reactant gases flow rate, silane to ammonia ratio and film deposition rate.

Collins et.al. [7] report the sum of silane and ammonia flow rates as a factor, most significantly affecting film deposition rate, while other factors having non-linear influence to it. Greater flow rates, as reported by the authors, also lead to the better stoichiometry of the film. However, another sources report the stoichiometry to be affected by the silane to ammonia ratio (Φ_{SiH4}/Φ_{NH3}) [2, 6, 8]. It is also reported the stoichiometry of the film to be strongly correlated ($r = 0.93$) with the refractive index [7]. This observation defines the refractive index to be easy

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determinable measure of the film quality: stoichiometric silicon nitride is nearly inert to the most common wet etchants, therefore higher refractive index defines more etch selectivity. The desirable value of silicon nitride refractive index at 632.8 nm is from 1.90 to 2.20.

Increase of gas flow ratio, increasing the film deposition rate, tends to decrease the stoichiometry, which is reflected by decreasing of refractive index and increasing of wet etch ratio. Similarly, PECVD silicon nitride deposition studies [2 – 8] report increase of the plasma power density to be related wit the higher film deposition rates (with non-linearities and/or saturation), causing poorer refractive index and etch rate. This is implicitly confirmed by the real-time quadruple mass spectrometry, performed by Knight et.al. [9], finding the increase of the refractive index of the film to be related with increase of disilane (Si_2H_6) content in plasma, which is inversely and non-linearly dependant on the plasma power.

The contribution of Kubacki [2] is about the large hydrogen content in the PECVD silicon nitride film, which causes the long term stability and reliability concerns. Author solves the problem by replacing ammonia in the gas mixture with the pre-ionized monatomic nitrogen. This results in low stress film with refractive index of 1.92, deposited over the substrate at room temperature.

Wang et.al. [4] increased the integrity of the deposited film by the means of dual frequency plasma and relatively high (550 °C) substrate temperature. Elevation of the substrate temperature by 150 °C results in decrease of hydrogen content by 50 %. Both dual plasma frequency and elevated substrate temperature resulted in very low etch rate of (25 – 28) Å/min.

Increase of the substrate temperature during the deposition is universally accepted as a mean to improve the stoichiometry of the film, decrease of the hydrogen content, decrease of the surface porosity and decrease of the intrinsic stress. However, recent advances in development of new modifications of silicon nitride synthesis technologies [5, 16 – 18] tend to develop film deposition strategies that preserve the high deposition rates, high film integrity and density when the substrate is at or nearly the room temperature. Nevertheless, in most of the cases it is related with the cumbersome technological solutions that unlikely are acceptable economically in our conditions.

The goal of this work was to research the properties of PECVD silicon nitride, deposited by the single wafer reactor. Films, produced by this reactor, are to be used for membranes of silicon micromachined capacitive ultrasound transducers [12 – 14].

DEPOSITION EQUIPMENT

The need to originally develop the PECVD reactor arises because of unavailability of single-wafer commercial products to be technologically feasible and economically reasonable for the forthcoming research. Single-wafer reactors are ideal for use in the development of semiconductor processes, the processing of large size wafers and the fabrication of advanced, low-volume integrated systems, such as in [5]. One of the goals of the experimental design was to extend the range of the feasible by the process engineers. Another purpose of the advanced design was to provide an exceptional monitoring and control abilities for the synthesis process.

In order to distribute a silane - ammonia reaction more evenly and deposit the film in the most effective way, a reactor design was developed (Fig. 1) whereby the gas mixture is supplied from the periphery of the bottom electrode and outflow is in the centre. The substrate is placed over the bottom electrode, which contains also the automatically controlled heater, capable to maintain stable substrate temperature up to 500 °C. The output of the 13.56 MHz RF generator is connected to the water cooled top electrode. The plasma power is to be manually adjusted from 0 W to 1000 W or controlled with the external process computer. Additionally, the plasma power density can be adjusted by alternating the distance between the electrodes from 10 mm to 60 mm. Three mass flow controllers maintain the flows of the reactant and diluting gases with the uncertainty interval of ±1.5 %. Gas flows are also possible to be regulated within the external control loop.

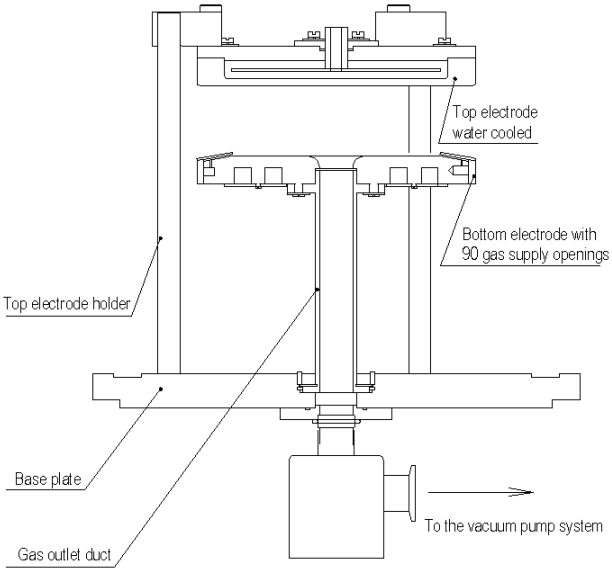

Fig. 1. Simplified drawing of PECVD reactor

Advances, carried by the exceptional process observability and controllability features are believed to be able to bring PECVD process to the new level of precision and repeatability. However, in this work only the functional correctness of above mentioned features was explored, leaving the closed loop control to be investigated further.

PROCESS PARAMETERS AND RESPONSES

The independent process parameters, potentially able to influence the properties of the resulting film, were chosen to be the reactant gases flow ratio Φ_{SiH4}/Φ_{NH3} and the plasma power. Other parameters that usually influence the synthesis process, such as diluting gas flow (Ar in our case), deposition chamber pressure (10 Pa) gap between the electrodes (50 mm) and the substrate temperature (350 °C) were kept unchanged.

The process responses measured were the growth rate, film thickness, refractive index (n), surface morphology parameters H_{mean} and R_a and film composition.

Film growth rate was estimated *in-situ*, following the interference color intensity and then verified *ex-situ* after the thickness measurement. The thickness and refractive index were measured by a laser ellipsometer (Gaertner L115, $\lambda = 632.8$ nm) at several different sites of three different radial positions. A non-uniformity of these properties was evaluated as a standard deviation.

The surface morphology of the films were estimated by the atomic force microscope (AFM, NT-206) working in contact mode. Statistical measures, related with the surface roughness, such as H_{mean} (representing average height of the bumps) and R_a (representing the arithmetic average of deviations from H_{mean}) were supposed to be the measures of film quality: lesser values are desirable.

Film composition was estimated by the X-ray photoelectronic spectrometry (XPS, XSAM800 Kratos Analytical).

RESULTS AND DISCUSSIONS

Some cases of dynamics of the film deposition, estimated in-situ, are presented in Fig. 2. The ratio of the reactant gases R was changed from 0.5 to 1.0. This caused the deposition rate to change from 20.2 nm/min to 32.7 nm/min (parameter S at the Fig. 2), correspondingly. The deposition was stopped after the evaluated thickness of the film reached 300 nm. After the ellipsometric verification an actual film thickness was found to be within ±15 % of that value. The non-uniformity of the film thickness and refractive index did not overcome the values of ±12 %, as measured in three different radial positions.

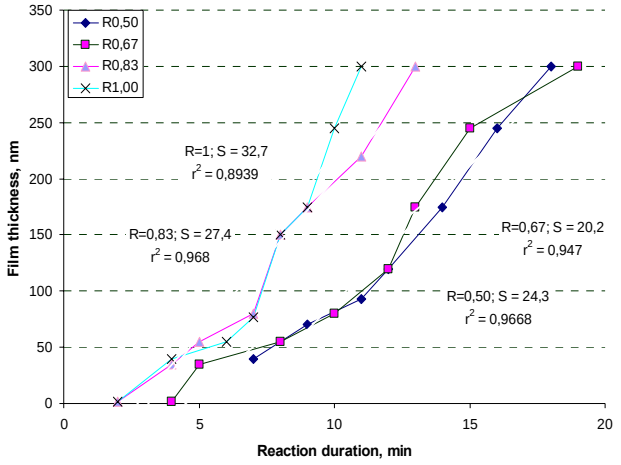

Fig. 2. Film deposition dynamics. Parameter R denotes the reactant gases flow ratio, S – characterizes the rate of the process, nm/min with the certainty of r^2

The influence of the plasma power on the refractive index of resulting film is presented in Fig. 3. Together with the plasma power the reactant gases ratio R was also slightly alternated, causing the values of the refraction index to be scattered.

Despite a trend of the refractive index to be decreased when the power increases, some maximum of the values in the region of 15 W can be observed. This could be taken as a presumable optimum, keeping in mind that other flow rates of the reactant gases are able to produce another optimum values, because overal electrical conductivity of plasma changes when the gas flows change.

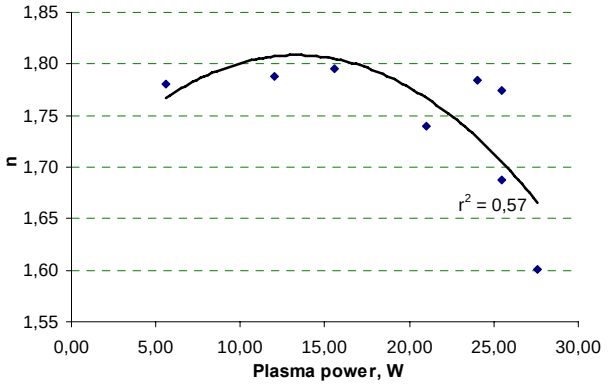

Fig. 3. Refractive index of silicon nitride film versus RF plasma power

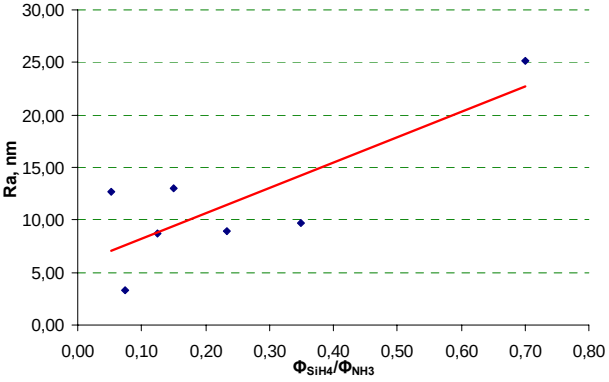

Fig. 4. Surface roughness of the silicon nitride film versus rectant gases flow ratio

The higher values of Φ_{SiH4}/Φ_{NH3} are also to be related with the poorer morphological characteristics of the film surface (Fig. 4). Although the desirable values ($R_a = 3.3$ nm; $H_{men} = 13.36$ nm, Fig. 5) were obtained at comparably low Φ_{SiH4}/Φ_{NH3} values (in the region of 0.1), causing low deposition rates (approximately 10 nm/min), it is still acceptable both technologically and economically.

XPS spectrometry, being the most cumbersome investigation in this work, was limited to comparison of two film samples, deposited with the new device to the etalon PECVD silicon nitride film.

We used as a reference the SiN sample produced by PK-2430PD (Plasma Therm. Incorp.) from the mixture of SiH_4, NH_3 and N_2 at $Tp = 300$ C, 0.25 W/cm^2, 0.5 torr. The samples investigated represent the boundary conditions with the values of $\Phi_{SiH4}/\Phi_{NH3} = 0.75$ (SiN007.3) to $\Phi_{SiH4}/\Phi_{NH3} = 1.25$ (SiN010.1) with the plasma power 25 ±2 W. After the Table 1, the case of SiN007.3, containing nearly reference concentration of silicon and nitrogen atoms, similarly with the case of SiN010.1, has much larger oxygen content. We assume this to be the influence of the residual oxygen at the deposition chamber.

Table 1. Film composition results delivered by XPS

Sample	Atomic concentrations, %			
	O_{1s}	N_{1s}	C_{1s}	Si_{2p}
Reference	34.27	13.49	26.48	25.77
SiN007.3	50.46	12.94	12.13	24.53
SiN010.1	58.26	2.07	16.57	22.92

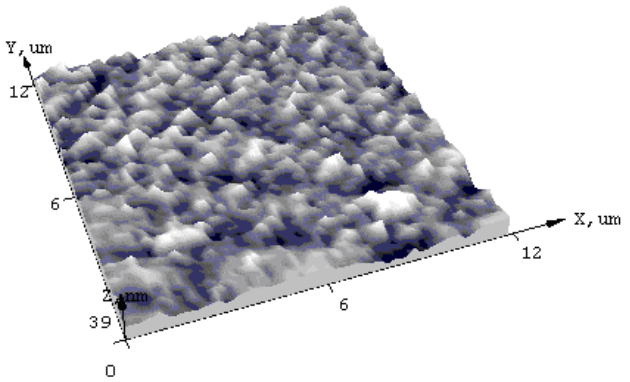

Fig. 5. 3D image of AFM scan of the film surface with R_a = 3.3 nm and H_{mean} = 13.36 nm

Moreover, SiN010.1, being deposited with the larger R, contains very little of nitrogen, therefore, the film, deposited at these conditions, presumably contains mainly the silicon oxides instead of nitrides. The spectrometry data correspond well with the refractive index measurement data: measured refractive index values are 2.01 ±0.20 and 1.56 ±0.14 in film with high and low content of nitrogen atoms, correspondingly.

CONCLUSIONS

In general we find the new equipment to be reliable enough to produce the PECVD silicon nitride films of desirable quality.

Ellipsometric measurements, which were of the largest part in this work, show that silicon nitride films with desirable thickness (0.3 μm – 0.5 μm) and refractive index (1.90 – 2.10) can be produced with the new deposition apparatus at explored conditions with maximum deposition rate of 25 nm/s.

The process parameters giving an optimum of the deposition rate and the film quality we define to be the value of the ratio of the reactant gases R between 0.65 and 0.75 and the plasma power between 18 and 25 W.

This also serves well in the terms of film surface quality: the measured values of H_{mean} and R_a for defined process parameters lay within the ranges of 13.4 nm – 55.0 nm and 3.3 nm – 13.5 nm, correspondingly, and this is fully acceptable for intended application.

Lower deposition rates also influence well the film composition, though the oxygen content has to be reduced.

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