Low temperature deposition of low stress silicon nitride by reactive magnetron sputtering

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Abstract. Silicon nitride thin film is a well-know kind of material in semiconductor industries. These films are used in important applications such as protective layers; insulators for optical devices, as dielectric material for thin film transistors (TFTs), etc. In this work, silicon nitride thin films were deposited at room temperature through of the reaction of sputtered silicon by argon ions and nitrogen gas with relatively high deposition rates in sputtering reactive processes. We have obtained silicon nitride thin films with low stress for MEMS (Micro Electro Mechanical Systems) fabrication and in post-processing of sensors and actuators devices. Silicon nitride thin films obtained in this work showed stoichiometric (Si3N4) and/or rich in silicon with low mechanical stress and good dielectric properties. The films were analyzed by scanning electron microscope, micro-Raman spectroscopy, profilometry, current-voltage (I-V) and capacitance-voltage (C-V) measurements, laser-based measurement for determination the internal stress and Rutherford Backscattering.

1. Introduction
Silicon nitride (Si3N4 or SiN x) is a very important ceramic due to its chemical, mechanical and electronic properties. It is chemically inert and show superior mechanical properties at high temperatures [1]. Silicon nitride is an important material in microelectronics due to its high resistivity, higher dielectric constant compared to silicon dioxide, mechanical strength, and chemical inertness. It is used as a gate insulator in thin film transistors that are in flat panel displays. It is also used in non-volatile memory devices because of its trapping ability. It can be applied as an oxidation mask and diffusion barrier in integrated circuit technology [2].

Silicon nitride films are mainly prepared by chemical vapor deposition (CVD) and plasma enhanced chemical vapor deposition (PECVD) [2-5]. Even though chemical vapor deposition is widely used for deposition of these films, the main disadvantages of this technique are the incorporation of hydrogen in the films and high substrate temperatures [6]. The entrapped hydrogen in the films can deteriorate the properties of silicon nitride, and the high substrate temperature is not generally desired in microelectronic applications [7].

Reactive Magnetron Sputtering [8-10] at low substrate temperature can provide silicon nitride films with extremely low hydrogen content [3]. In this work, we have obtained silicon nitride films...
deposited by Reactive Magnetron Sputtering with low temperature deposition, low stress and low hydrogen content for MEMS (micro electro mechanical systems) fabrication [11-12]. Thus, flexibility in controlling the flux and energy of the ions will facilitate the growth of thin films with desired properties.

In this article we discuss the properties of silicon nitride films prepared by Reactive Magnetron Sputtering. The properties are studied using micro-Raman spectroscopy [13], profilometry, laser-based measurement for determination the internal stress [14-15], scanning electron microscopy [16] and Rutherford Backscattering spectrometry [17] and current-voltage (I-V) and capacitance-voltage (C-V) measurements [18].

2. Materials and methods

2.1. Deposition system

The silicon nitride films were deposited in a magnetron sputtering plasma system. We used a silicon target and nitrogen and argon as the process gases. The pressure was fixed in 5 mTorr while the applied power was varied (250 W and 350 W) and the process time was varied too (from 10 min until 120 min). For obtaining a step in a silicon nitride films for measuring the thickness a mechanical mask was used (protecting a small area in the surface samples).

2.2. Samples

The substrates used to deposit the films were three-inch diameter silicon wafers, 380 µm thick and orientation (100). They were submitted to a Piranha clean followed by a diluted HF dip, before the films deposition. The silicon nitride films were deposited at room temperature with relatively high deposition rates.

2.3. Techniques of analyses

For evaluating the deposition rates, we measured the silicon nitride thickness using a Dektak 3030 profilometry from Sloan-Veeeco. For analyzing the surface topography and the profiles of the samples we used a FEI NOVA nano400 scanning electron microscope (SEM).

We analyzed the films with a vis-UV Raman spectrometer system (Renishaw micro-Raman 2000 spectrometer on a 40x objective with a photomultiplier). Unpolarized Raman spectra were acquired at $\lambda=514.6$ nm, the spectral resolution was about 4-6 cm$^{-1}$ and the power on the sample was kept well below 1 mW.

The Si/N ratio was analyzed by Rutherford Backscattering Spectrometry (RBS). The total stress of the silicon nitride films was obtained using a KLA-Tencor FLX stress measuring system. For electrical measurements metal/nitride/silicon capacitors were formed by thermal evaporation of 300 nm thick aluminium films. The capacitors were patterned with a mask composed of 700 µm pads. On the wafer backside was evaporated a 300 nm thick Al film. C-V measurements at 1 MHz were made to determine the dielectric constant and I-V measurements were made to determine the dielectric breakdown electric field and conductivity. The results obtained are shown in this work.

3. Results and discussion

Firstly, we have made a plasma composition effects study to verify the influence of this parameter in the deposition rate, in the Si/N ratio and in the electrical properties. For this, the deposition time (30 min and 60 min) and the applied RF power (250 W and 350 W) were varied. The plasma composition effects in these parameters can be observed in figures 1, 2 and 3.

Observing figure 1, we can notice that the deposition rate decreases with the nitrogen addition in the argon plasma. This effect occurs due the lesser collision section of the nitrogen ions, when we compared with the collision section of the argon ions. Thus, lesser material removal of the target occurs when more nitrogen is present. In general, the thickness increases with the increase of deposition time and the applied RF power (as we can see in figure 2).
Figure 1. Deposition rate.

Figure 2. Thickness variation.

Figure 3. Si/N ratio.
The most stoichiometric silicon nitride films (Si₃N₄) were obtained for plasma processes with nitrogen content of 40% and content argon of 60%, and with applied FR power of 250W. The process parameters effect in the dielectric constant and the stress of the silicon nitride is presented in figures 4 and 5, respectively.

![Figure 4. Dielectric constant.](image)

![Figure 5. Stress of the silicon nitride films for 40% Nitrogen content.](image)

The most stoichiometric silicon nitride films (Si₃N₄) presented a dielectric constant of 7.0 (see figure 5). In general, silicon nitride films obtained with high nitrogen content present low mechanical stress. Thus, for measuring the mechanical stress of the silicon nitride films we have selected films with high nitrogen content and the nitrogen content was not varied (fixed at 40%) and the deposition time and the applied RF power were varied (see figure 5).

Observing the figures, we can notice that the deposition rate decreases when the deposition time is increased. This effect occurs due the increase of the density of the silicon nitride films and the better accommodation of the atoms in the films. So, the mechanical stress decreases.

In such a way, these films can be applied in MEMS fabrication and as mask to KOH etching, how we can see in figure 6 that shows a silicon structure with silicon nitride rich in silicon as mask. The silicon nitride films obtained in this work showed low mechanical stress, high nitrogen content, good dielectric constant and high deposition rate at room temperature.
Figure 6. Silicon structure with silicon nitride rich in silicon as mask.

4. Conclusions
In this work, we have obtained silicon nitride thin films at room temperature at relatively high deposition rates with sputtering reactive plasma processes. The films showed good stoichiometry (Si$_3$N$_4$) and/or rich in silicon with low mechanical stress and good dielectric properties. Consequently, the silicon nitride films can be used for MEMS fabrication, electrical insulators, and gate dielectric in thin films transistors (TFTs), diffusion mark and KOK mask, etc. Thus, the silicon nitride films obtained in this work can be used in different technological areas.

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