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Microelectronic Engineering 77 (2005) 144–149
MICROELECTRONIC ENGINEERING
www.elsevier.com/locate/mee

Study of PECVD SiO_xN_y films dielectric properties with different nitrogen concentration utilizing MOS capacitors

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Received 12 July 2004; accepted 5 October 2004
Available online 19 October 2004

Abstract

In this work metal/oxide/semiconductor (MOS) capacitors with different nitrogen content SiO_xN_y gate dielectric are fabricated and characterized. The dielectric films are deposited by the plasma enhanced chemical vapor deposition technique from N_2, N_2O and SiH_4 gaseous mixtures at low temperatures.

The MOS capacitors were characterized by low and high frequency capacitance (C–V) measurements, from where the interface state density (D_{it}), the effective charge density (N_{eff}) and the dielectric constant (k) were extracted.

The results show a dielectric constant varying linearly in function of the films nitrogen concentration, from a value of 3.9, corresponding to SiO_2 to 7.2, corresponding to Si_3N_4.

We observed a variation of D_{it} in function of the films nitrogen concentration, the smallest obtained value corresponding to the Si_3N_4 film ($\sim 1 \times 10^{11}$ cm^{-2} eV^{-1}), however this film presents higher leakage current density than others. In order to optimize both parameters a double dielectric layer is proposed, a first layer of Si_3N_4 film, which presents the highest dielectric constant and best interface properties, and a second layer of SiO_xN_y with high nitrogen concentration, in order to maintain the equivalent dielectric constant high but minimizing the leakage current problems.

Keywords: Plasma enhanced chemical vapor deposition; Silicon oxynitride; Metal/oxide/silicon capacitors

1. Introduction

Metal/oxide/silicon (MOS) technology is based on thermally grown SiO_2, as gate dielectric material, due to its high reliability and very low interface defect density, high resistivity, excellent dielectric strength and a large band gap [1–3]. However, in recent years, with the development of the ULSI technology, high-temperature processing needs to be minimized and, consequently, considerable attention has been focused on the search for dielectric films produced at low

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0167-9317/$ - see front matter
doi:10.1016/j.mee.2004.10.002

temperatures to replace the conventional material. Thus, films produced by the plasma enhanced chemical vapor deposition (PECVD) technique are very attractive due to the low processing temperatures [4–7].

The SiO_2 thickness is continuously decreasing, due to the need of high dielectric capacitance values to produce the required drive currents for submicron devices, and it is approaching its thinning limit of ~1 nm [1,2,8] It is because, for SiO_2 films with thickness smaller than 3 nm, tunneling currents, which increase exponentially for decreasing SiO_2 thickness, become significant [1]. The SiO_2 ultra-thin dielectric layer gives rise to some problems such as low barrier to boron penetration in the dielectric material, which comes about when p+ polysilicon is used as gate contact in p-MOSFET's, shifting the threshold voltage of the device [1,8–11]. Furthermore, for SiO_2 films with thickness smaller than 3 nm, tunneling currents, which increase exponentially for decreasing SiO_2 thickness, become significant [1].

To overcome these problems, research is now directed to the substitution of SiO_2 by high-k materials making possible the use of thicker films maintaining the capacitance associated to a SiO_2 thin-film ($k = 3.9$) [1,2]. These high-k dielectric materials are deposited by several techniques, chemical vapor deposition (CVD), jet vapor deposition (JVD), atomic layer deposition (ALD), Sputtering among others. Some of these materials, as TiO_2, ZrO_2 and HFO_2 have high dielectric constant values (80–100) but they present some problems when utilized as gate dielectric film, such as: high leakage current, poor Si interface quality and low thermodynamic stability [1]. An alternative material, in spite of its relatively low dielectric constant (4–7), is SiO_xN_y because it is totally compatible with the silicon MOS technology and exhibits enhanced resistance to high field stress, enhanced hot carrier immunity, resistance against dopant penetration, higher dielectric strength and higher dielectric constant over conventional SiO_2 [1,2,6,8,10,12,13]. Different techniques are used to obtain SiO_xN_y films. Nitrogen can be incorporated in SiO_2films utilizing thermal oxynitridation, annealing treatments in nitrogen environment, thermal nitridation in ammonium environment or by chemical or physical deposition techniques. The thermal oxynitridation is performed in NO or N_2O environments at high temperatures (700–1000 °C), also annealing treatments of SiO_2 in N_2 environment utilize temperatures higher than 950 °C and long processing time (>1 h). However these techniques do not permit high nitrogen incorporation (less 10%). In order to obtain higher nitrogen concentration deposition techniques should be utilized, among them we can mention PECVD, LPCVD, APCDV, JVD. From these PECVD is advantageous due to the low deposition temperature (<320 °C) and because it enables a good control of the chemical composition by the deposition parameters.[5,14]. Recent works on PECVD SiO_xN_y, aiming to utilize these films in optical waveguides, MOEMS and in MOS devices, have reported good control of the dielectric constant with the deposition conditions, however the interface properties are far from device quality only with pre-oxidation and post-annealing treatments the interface state density reaches the 10^{10} cm^{-2} eV^{-1} range [6,15–17].

In previous works [18–20] we have shown that simply by varying the N_2O/SiH_4 flow ratio variable composition SiO_xN_y films are obtained, though limited to a maximum N concentration of ~15%, also better interface properties than SiO_2 are obtained for the SiO_xN_y films. In this work SiO_xN_y films, with higher nitrogen concentration, going from 0 to 55 at.%, are utilized as insulating layer to fabricate MOS capacitors and the effect of the nitrogen incorporation on the device characteristics is analyzed.

2. Experiment

2.1. Films deposition

The films were deposited by the PECVD technique from silane, nitrous oxide and nitrogen gaseous mixtures, in a rf (13.56 MHz) capacitively coupled reactor. The details of the PECVD system are reported by Carreño et al. [21]. Films with different nitrogen, silicon and oxygen content were obtained by varying the N_2 and N_2O flows, maintaining the $N_2 + N_2O$ flow at 75 sccm and the SiH_4

one at 15 sccm utilizing a RF power of 200W (high rate deposition) for the first set of MOS capacitors, and $N_2 + N_2O$ flow of 39 sccm and a SiH_4 flow of 3 sccm utilizing a RF power of 100 W (low rate deposition) were used for the second MOS capacitors set. All the samples were deposited at 320 °C, since our previous experiments indicate this is the optimum temperature to prevent Si–OH bonds [22].

The deposition parameters for the samples studied in this work are shown in Table 1. Single crystalline silicon substrates (1 0 0) orientation were utilized for thickness and refractive index characterization. For the Rutherford backscattering spectroscopy (RBS) measurements the films were deposited onto ultra dense amorphous carbon.

The refractive index and the thickness of the samples were obtained by ellipsometry measurements performed in a Rudolph Research Auto E1 equipment having a He–Ne laser (632.8 nm) as light source. The measurements were done on different points of the films to determine the standard deviation of the refractive index and thickness along the sample. The thickness was also measured in an Alpha Step 500 Tencor surface profiler. The amount of Si, N and O per unit area (atoms cm^{-2}) was obtained by RBS experiments at LAMFI/USP, Sao Paulo, using a He^+ beam with an energy $E = 1.7$ MeV, a charge $Q = 30$ μC, a current $I = 30$ nA and a detection angle $\theta = 170°$.

Table 1
Dielectric film deposition conditions

Sample set	F (N_2:N_2O:SiH_4) sccm	Deposition rate A/min	Refractive index (n) ± 0.002	N (at.%) ± 2%
1	00:75:15	171	1.469	0
	30:45:15	221	1.541	6
	45:30:15	240	1.613	18
	60:15:15	234	1.717	31
	75:00:15	185	1.979	55
2	00:39:03	21.60	1.485	0
	32:07:03	39.80	1.558	9
	34:05:03	31.03	1.602	24
	36:03:03	38.83	1.690	28
	39:00:03	30.62	1.912	53

2.2. MOS capacitors fabrication

Two sets of MOS Capacitors were fabricated on p-type (1 0 0)-oriented silicon wafers with resistivity in the 1–10 Ω cm range. The silicon substrates were chemically cleaned by standard RCA procedure and subsequent etching in diluted HF solution to remove the native SiO_2 layer. In sequence ~100 nm SiO_xN_y insulating layer was deposited by PECVD from SiH_4, N_2O and N_2 gaseous mixtures without further thermal annealing. The metallic contacts for all of the studied capacitors were made by the sputtering technique depositing 300 nm of Al. The 9×10^{-4} cm^2 capacitor contact area was defined by photolithography and subsequent chemical etching, the contacts were annealed in forming gas atmosphere (4% of H_2 and 96% of N_2) at 450 °C for 30 min.

The high (1 MHz) and low frequency *C–V* curves were measured with a Keithley model 82–DOS Simultaneous *C–V* equipment. From these curves, the series resistance, the dielectric constant, the effective charge in the insulator layer, the interface trap density and the dielectric layer thickness were calculated.

3. Results and discussions

In Fig. 1 we present the interface state density for the first and second sample sets as function of the nitrogen concentration in the dielectric layer.

We can observe that both capacitors sets present the same behavior, the D_{it} increases reaching the maximum value and for higher nitrogen content the D_{it} decreases reaching the minimum value for the silicon nitride type film. The lower D_{it} values were found for high rate samples set, probably due to fact that to low rate deposition leads to a higher interface stress. The variation found in D_{it} values as function of nitrogen concentration in the films can be attributed to changes in internal stress or to different structural order. It can be observed that the smaller values were obtained for pure SiO_2 and for stoichiometric Si_3N_4 films, which present more structural order than the other films, for the other compositions an alloy material is obtained thus

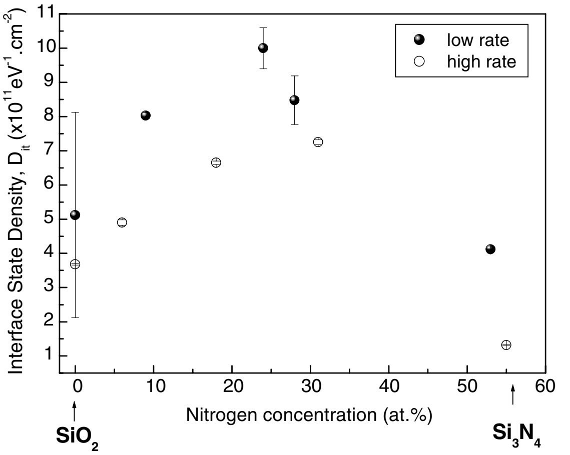

Fig. 1. Interface state density (D_{it}) as function of dielectric nitrogen concentration.

increasing the chemical and structural disorder. The minimum D_{it} value obtained for the Si_3N_4 film can be due to the lower stress associated to this material, in previous works we observed that Si_3N_4 presents less internal stress than SiO_2. These results are promising and comparable with results reported in the literature for dielectric materials obtained with other techniques (as LPCVD – 800 °C [23] and thermal oxynitridation – 1100 °C [24]) indicating that PECVD is a good alternative for low temperature dielectric production.

In Fig. 2, the effective charge density behavior as function of the nitrogen concentration for both sample sets is shown. It is observed that it remains almost constant, that is to say, this parameter is not being influenced by the nitrogen concentration in the film. Also, as the values are high it might by that the nitrogen influence is masked by the effect of contamination, which can take place either during processing or during deposition.

In Fig. 3 the leakage current density as function of films nitrogen concentration for both sample sets is depicted. It can be appreciated that its value remains almost constant for all sample except for the Si_3N_4 film, which suffers a low increase. Also it is seen that low deposition rate films exhibit lower leakage current density, which can be attributed to the lower pinhole density due to the lower deposition rate.

The dielectric constant increases for increasing nitrogen concentration, as expected. Even more, the results in Fig. 4 show that the dielectric constant varies linearly with nitrogen concentration, from ~3.5 for SiO_2 to 7.2 for Si_3N_4.

In Fig. 5 we present the refractive index, obtained by ellipsometry, as function of the dielectric constant (k) square. It can be observed that the dielectric constant value is varying linearly with n^2, indicating that these materials obey the dielectric materials expression ($n = q\sqrt{k}$), and that the

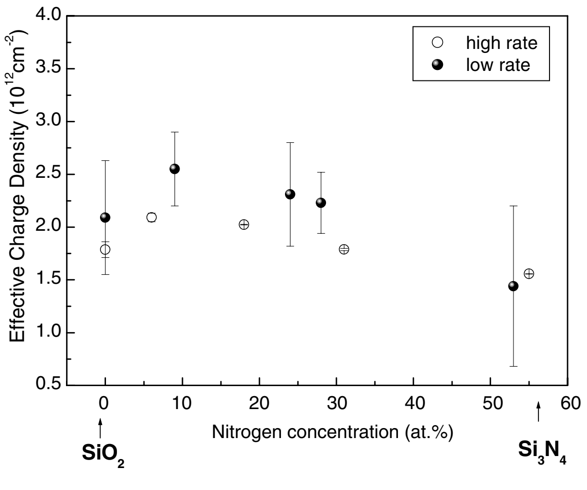

Fig. 2. Effective charge density (N_{eff}) as function of dielectric nitrogen concentration.

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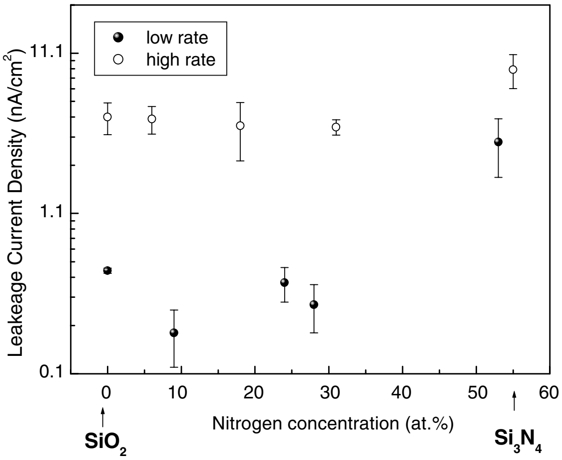

Fig. 3. Leakage current density (Iq) as function of dielectric nitrogen concentration.

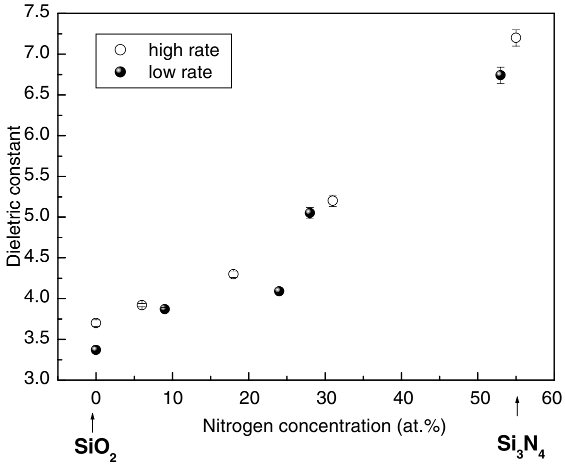

Fig. 4. Dielectric constant (k) as function of the dielectric nitrogen concentration.

dielectric constant depend only on the nitrogen concentration in the SiO_xN_y film.

The higher obtained dielectric constant value was ~7.2 for the Si_3N_4 material which also presented the lower interface state density. However this material presented higher leakage density current than the others. In this way, in order to optimize all the parameters, a double layer (Si_3N_4/SiO_xN_y) can be utilized, where the Si_3N_4 ($k \sim 7$) should be the first layer, because of its better interface properties, and SiO_xN_y with $k \sim 5.5$,

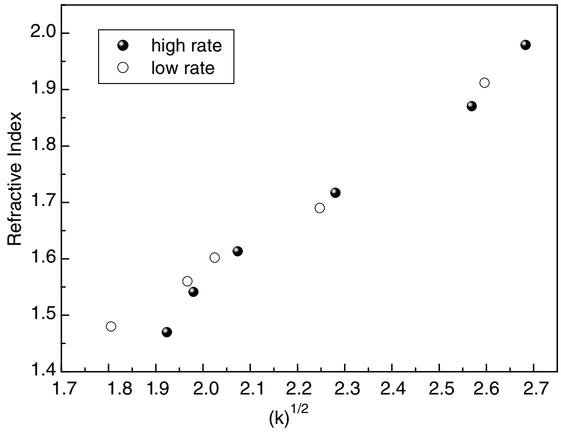

Fig. 5. Refractive Index (n) as function of the square root of the dielectric constant $(k)^{1/2}$.

could be the second layer since it still presents high nitrogen content but lower leakage current density. With this choice the equivalent dielectric constant is still higher than for conventional SiO_2 film and exhibits better interface properties.

4. Conclusions

MOS capacitors utilizing SiO_xN_y films with nitrogen concentration, varying from 0 to 55 at.%, deposited by the plasma enhanced chemical vapor deposition (PECVD) technique as gate dielectric, were fabricated and characterized. The results show that the dielectric constant varies linearly with the films nitrogen concentration, from ~3.5, corresponding to SiO_2 to 7.2 corresponding to Si_3N_4. A variation in the interface state density (D_{it}) with the films nitrogen concentration is observed, the smallest value is obtained for the silicon nitride dielectric layer, however this film presents higher leakage current density than the others. In order to optimize the parameters a double dielectric layer is proposed, first a Si_3N_4 film, which presents the highest dielectric constant and best interface properties, and a second layer of SiO_xN_y with a high nitrogen concentration, in order to maintain the equivalent dielectric constant high, but minimizing the leakage current problems, making it a good candidate for SiO_2 substitution.

Acknowledgments

The authors are grateful to the Brazilian agencies FAPESP and CAPES for financial support and thank the contributions of Ms. D. Criado for the preparation and physical characterization of the samples.

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