Electrical and infrared characterization of thin SiO_2 films deposited by r.f. magnetron sputtering[♣]

N. NEDEV[*], E. MANOLOV[a], D. NESHEVA[a], J. M. TERRAZAS, B. VALDEZ, M. A. CURIEL, R. ZLATEV
Instituto de Ingenieria,Universidad Autónoma de Baja California, Benito Juárez Blvd., s/n, C.P. 21280, Mexicali, Baja California, México.
[a]*Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria.*

SiO_2 films deposited by reactive r.f. magnetron sputtering at two applied powers, 420 and 560 W, and at partial pressure ratios between oxygen and Ar in the range 1 - 0.1 are studied. FTIR spectra show that all films have compositions close to the stoichiometric one. High temperature annealing at 1000^{o}C shifts the band due to the Si-O-Si symmetric stretching vibration to values typical of stoichiometric SiO_2. The MOS structures with SiO_2 deposited at P = 420 W and a gas pressure ratio R = 1 have lower densities of defects at the SiO_2/c-Si interface than those deposited at the same R but at P = 560 W. For both series of samples, a decrease in the oxygen partial pressure leads to an increase in the interface defect density. In all MOS structures, the main component of the current flowing through the oxide at electric fields higher than 4 MV/cm is due to Fowler-Nordheim tunnelling.

(Received November 5, 2008; accepted December 15, 2008)

Keywords: Sputtered SiO_2 films, Electrical properties, IR, EDX, C-V, I-V

1. Introduction

Sputtering is a low temperature process, widely used for deposition of dielectric layers. Because of the low deposition temperature, sputtered silicon oxide films are interesting for application in thin film transistors [1,2] and as gate dielectrics in field effect transistors [3,4].

The great flexibility of the sputtering process makes it also attractive for the fabrication of MOS structures having gate stacks containing silicon nanocrystals (Si NCs) [5]. The film composition can be varied by varying the ratio between oxygen and argon in the deposition chamber. Sputtered SiO_2 films have been successfully used [6-9] to insulate Si NC layers from the control gate in MOS structures suitable for memory device applications.

It is known that the growth rate, and therefore the properties, of the sputtered films depend on the target power or bias voltage. In this work, we present results for sputtered SiO_2 films deposited at two values of the applied power and at various partial pressure ratios between the working gases, oxygen and argon.

2. Experimental details

Silicon oxide films with thicknesses in the range 25 - 60 nm were deposited by reactive r.f. magnetron sputtering of a Si target on top of p-type (1 Ω cm) or n-type (4 - 6 Ω cm) crystalline silicon. Two series of samples were fabricated: at applied high voltages of 1.5 kV and of 2 kV, i.e. at applied powers of P = 420 or 560 W, respectively. In the first series, the partial pressure ratio between oxygen and argon $R = p(O_2)/p(Ar)$ was varied in the range 1 - 0.1, while in the second series it was in the range 1 - 0.25. All depositions were at a total pressure of 30 mTorr. After the deposition, half of the samples were annealed at 1000 ^{o}C in a N_2 atmosphere for 60 min. For electrical characterization, Al metallization was carried out through a mask and MOS capacitors with areas of 2×10^{-3} cm^{-2} were formed. Aluminium was also used as a back contact to the crystalline silicon.

Energy Dispersive X-ray (EDX) spectra were measured using a Scanning Electron Microscope, JEOL, model JSM 6360, equipped with an EDX detector for spectral analysis, and semi-quantitative data about the chemical composition of the layers were obtained. The infrared spectra measurements were carried out using a Perkin Elmer Spectrum One FTIR spectrometer. The high frequency capacitance was measured by a HP4280A meter

[♣] Paper presented at the International School on Condensed Matter Physics, Varna, Bulgaria, September 2008

and the current-voltage characteristics by HP 3458A and FLUKE 5720A voltage source.

3. Results and discussion

Fig. 1 shows the FTIR transmittance spectra of non-annealed samples deposited at R = 1 and at both powers used. Also, the spectrum of a sample deposited at 420 W and annealed at 1000°C is shown. The peaks at ~ 612 and ~ 740 cm^{-1} are attributed to two different vibration modes of Si-Si bonding [10,11], while the third band with a peak in the 1065-1090 cm^{-1} range is due to a Si-O-Si symmetric stretching vibration, indicating that the samples have a composition close to the stoichiometric one [10-12]. In the case of as-deposited samples, the position of the third peak is at slightly lower wavenumbers with respect to silica, at ~ 1065 cm^{-1} for 420 W sample (curve 1) and at 1073 cm^{-1} for 560 W sample (curve 3). Such a "red" shift is related to a lower oxygen content than the stoichiometric one [13]. After thermal annealing, the band shifts to values typical for stoichiometric SiO_2, 1079 cm^{-1} for the 420 W sample (curve 2) and 1080 cm^{-1} for the 560 W sample (not shown).

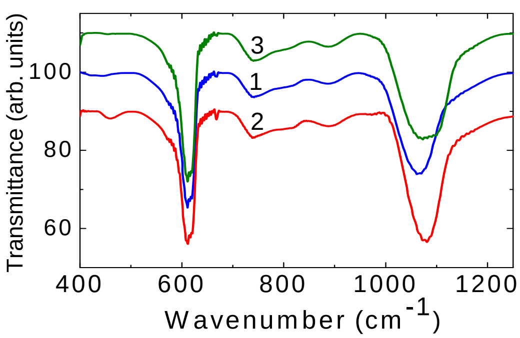


Fig. 1. FTIR transmittance spectra of non-annealed oxide layers deposited at 420 W (curve 1) or 560 W (curve 3) and R = 1 and of annealed SiO_2 deposited at 420 W and R = 1 (curve 2).

Fig. 2 shows the EDX spectra of a non-annealed and annealed oxide film deposited at R = 1 and an applied power of 420 W. Similar spectra were obtained for all samples used in this study. After obtaining the EDX spectrum, atomic and weight concentrations were estimated [14]. For all layers deposited at lower power and R in the range 1-0.1, an excess oxygen concentration was found, 9-5 at. % above the stoichiometric one, while for the layers deposited at higher power and R in the range 1-0.25, the oxygen concentation was only slightly above the stoichiometric one (~2-1 at. %). After high temperature annealing, the oxygen concentration of the two types of layer (P = 420 and 560 W) decreased by ~1-2 at %, while the concentration of Si increased by the same value. Although the EDX results are in agreement with those obtained by IR spectroscopy, especially for the high power samples, a more precise technique is necessary for determination of the exact elemental concentrations.

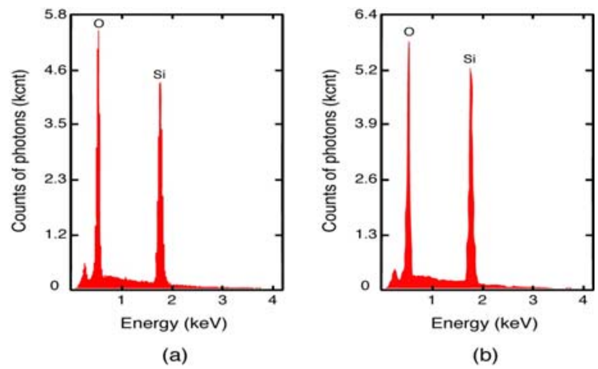
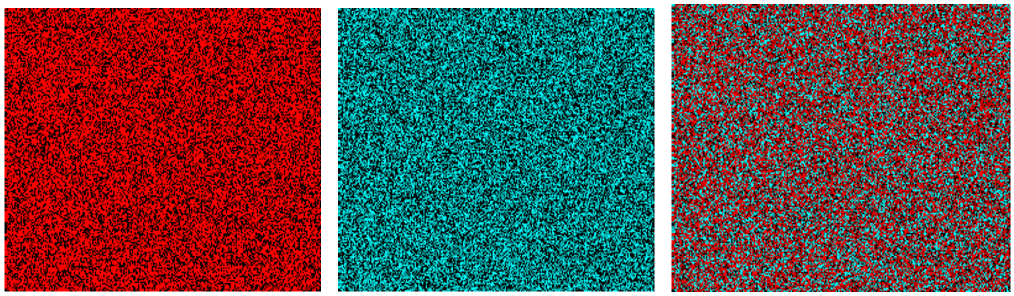


Fig. 2. EDX spectra of non-annealed (a) and annealed (b) samples deposited at P = 420 W, R = 1.

Figs. 3 (a), (b) and (c) present results on the distribution of oxygen and silicon in a non annealed sample deposited at R = 1 and an applied power of 420 W, obtained by EDX analysis. The analyzed area was 0.3 mm^2. Homogeneous distributions and overlapping are observed for this, as well as for all other, samples.

Figs. 4 (a) and (b) depict the high frequency capacitance-voltage (HF C-V) dependencies of non-annealed and annealed MOS structures with a SiO_2 layer deposited at R = 1 or 0.25, and P = 560 W. For both R values, counter clockwise hysteresis, due to parallel shift of the C-V curve, is observed. The hysteresis window of the as-deposited sample with R = 1 is about 0.4 V, while that of the sample with R = 0.25 is ~ 0.15 V for bias scans in the range ± 5 V. This result implies a lower density of bulk defects in the oxide layer deposited at R = 0.25.

On the other hand, the C-V curves of the structures with SiO_2 deposited at R = 1 are much steeper than those of structures with an oxide deposited at a lower R, which indicates a lower defect density at the SiO_2/c-Si interface [15].



(a) (b) (c)

Fig. 3. EDX maps of silicon (a) and oxygen (b) and their overlapping (c). SiO_2 deposited at P = 420 W and a partial pressure ratio of R = 1.

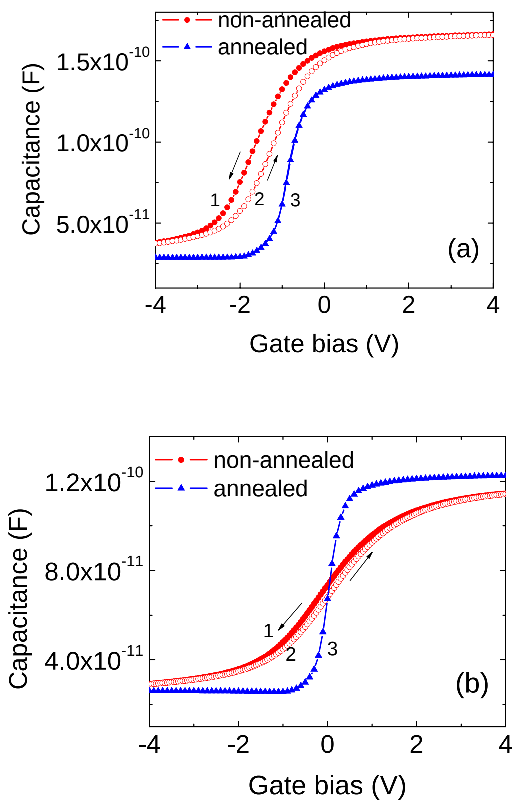


Fig. 4. HF C-V curves measured at 1MHz of non-annealed (curves 1, 2) and annealed (curve 3) MOS structures with a SiO_2 layer deposited at R = 1 (a), R = 0.25 (b) and P = 560 W.

The high temperature treatment leads to annealing of the bulk defects present in the oxide layer, proved by the absence of hysteresis in the C-V curves for both R = 1 (Fig. 4a, curve 3) and R = 0.25 (Fig. 4b, curve 3) samples, measured in the ± 10 V scan range. Another positive effect of the thermal annealing is the reduction in theSiO_2/c-Si interface defect density, demonstrated as an increase of the C-V curve slope. Also, a strong decrease in the parallel conductance of the annealed samples is observed, which confirms the annealing of the interface defects [16].

Fig. 5 shows the normalized C-V dependencies of non-annealed MOS structures with SiO_2 deposited at P = 420 W and R = 1 or 0.1. Both types of MOS structure have a C-V hysteresis window of about 0.5 V. Nevertheless, the oxide film deposited at the gas pressure ratio R = 1 has a much smaller value of the fixed oxide charge, demonstrated by a smaller value of the flat-band voltage and a much steeper C-V curve, indicating a better SiO_2/c-Si interface.

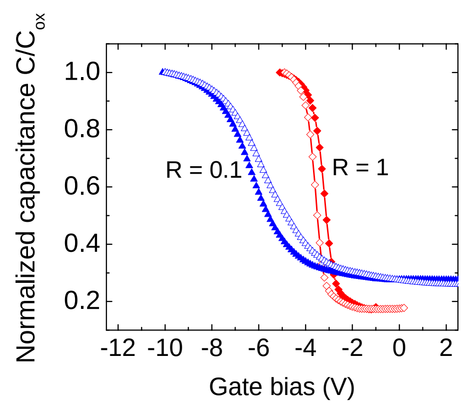


Fig. 5. Normalized HF C-V dependencies of MOS structures with SiO_2 deposited at R = 1, 0.1 and P = 420 W.

For all samples deposited at the applied power P = 420 W, high temperature annealing reduces the density of fixed charge, as is proved by the absence of hysteresis in the C-V curves. However, it does not lead to an increase in the curves slope, i.e. to improvement of the SiO_2/c-Si interface.

In Fig. 6, results for the current flowing through MOS capacitors with non-annealed oxide layers are presented. At weak electric fields, the I-V curves have different shapes, depending on the deposition conditions. Nevertheless, at electric fields > 4 MV/cm, a strong increase in the current is observed, presented by the straight lines in Fig. 6. Hence, at high electric field, the main conduction mechanism through all films deposited at both applied powers used in this study and at various gas ratios is Fowler-Nordheim tunnelling.

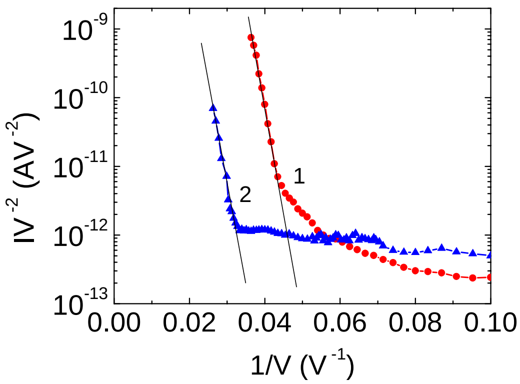


Fig. 6. Positive bias I-V characteristic of non-annealed MOS structures with SiO_2 deposited at R = 0.1, P = 420 W (curve 1) and R = 1, P = 560 W (curve 2) in coordinates corresponding to Fowler-Nordheim tunnelling.

4. Conclusions

FTIR spectra of silicon oxide layers deposited by reactive r.f. magnetron sputtering at two applied powers (P = 420 and 560 W) and at partial pressure ratios varied in a wide range show that the films have compositions close to the stoichiometric one. After high temperature annealing, the band due to Si-O-Si symmetric stretching vibration was shifted to values typical of stoichiometric SiO_2 (~ 1080 cm^{-1}).

The MOS structures with SiO_2 deposited at an applied power of P = 420 W and a gas pressure ratio of R = 1 have lower densities of defects at the SiO_2/c-Si interface than those deposited at the same R but at P = 560 W. For both types of sample, a decrease in the oxygen partial pressure leads to an increase in the interface defect density. Also, the two types of oxide have bulk defects in the oxide layer demonstrated by hysteresis in the high frequency C-V curves.

The main component of the current flowing through MOS capacitors with sputtered SiO_2 at electric fields higher than 4 MV/cm is due to Fowler-Nordheim tunnelling.

High temperature annealing strongly improves the properties of the oxide layers deposited at P = 560 W, regarding density of defects in the film as well as at the SiO_2/c-Si interface. Such SiO_2 films are suitable for application in MOS structures containing one or several SiO_2 layers with Si nanocrystals, attractive for the fabrication of non-volatile memory devices.

Acknowledgements

This study was supported by the Bulgarian Ministry of Education and Science under contracts F-1504 and NT-4-1 and Secretaria de Educación Publica through SEP-PROMEP Program, Mexico.

References

[1] S. Serikawa, F. Omata, IEEE Electron Device Lett. **20**, 574 (1999).
[2] S. Serikawa, F. Omata, IEEE Trans. Electron Dev. **49**, 820 (2002).
[3] E. V. Jelenkovic, K. Y. Tong, M. C. Poon, J. S. L. Wong, Semicond. Sci. Technol. **9**, 1673 (1994).
[4] E. V. Jelenkovic, K.Y. Tong, J. Vac. Sci. & Technol. B: Microel. Nanom. Str. **15**, 209 (1997).
[5] J. U. Schmidt, B. Schmidt, Mat. Sci. Eng. B **101**, 28 (2003).
[6] N. Nedev, D. Nesheva, E. Manolov, R. Brüggemann, S. Meier, K. Kirilov, Z. Levi, J. Optoelectron. Adv. Mater. **9**, 182 (2007).
[7] D. Nesheva, N. Nedev, E. Manolov, I. Bineva, H. Hofmeister, J. Phys. Chem. Solids **68**, 725 (2007).
[8] N. Nedev, M. Stoytcheva, D. Nesheva, E. Manolov, R. Brüggemann, S. Meier, Z. Levi, R. Zlatev, B. Valdez, L. Alvarez, in Proc. NSTI Conf., Santa Clara, CA (2007), Vol. **4**, p. 485.
[9] N. Nedev**,** D. Nesheva, E. Manolov, R. Brüggemann, S. Meier, Z. Levi, R. Zlatev, Journal of Physics: Conference Series **113**, 012034 (2008).
[10] Yu. Zhenriu, M. Aceves-Mijares, E. Quiroga, R. López, J. Carrillo, C. Falcony, J. Applied Phys. **100**, 013524 (2006).
[11] M. I. Alayo, I. Pereyra, W. L. Scopel, M.C.A. Fantini, Thin Solid Films **402**, 154 (2002).
[12] F. Ay, A. Aydinli, Optical Materials **26**, 33 (2004).
[13] D. V. Tsu, G. Lucovsky, B. N. Davidson, Phys. Rev. B **40**, 1795 (1989).
[14] EDAX, Genesis User's Manual, USA, EDAX (2002).
[15] S. M. Sze, Physics of Semiconductor Devices, Wiley, New York (1981).
[16] E. H. Nicollian, J. R. Brews, MOS Physics and Technology, Wiley, New York (1982).

*Corresponding author: nicola@iing.mxl.uabc.mx