

Role of ions in SiO₂ deposition with pulsed and continuous helicon plasmas*

Christine Charles[‡]

Plasma Research Laboratory, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, ACT 0200, Australia

Abstract: Good-quality silicon dioxide films have been deposited at low temperature (≤ 200 °C) using continuous and pulsed oxygen/silane plasmas coupled in a high-density, low-pressure helicon reactor. Although the total ion flux determines many of the structural properties of the deposited oxide, we have found that silicon-containing ions contribute to the film growth (up to 50 %) and appear to be responsible for the measured compressive stress.

INTRODUCTION

There has been increasing interest in the use of the plasma technology on silicon for the fabrication of optical devices, such as buried-channel planar optical waveguides, for telecommunication networks [1,2]. The deposition of the waveguide buffer, core, and cladding layers can be performed by using the ion-rich helicon radio-frequency source [3] where a continuous or pulsed plasma is used to break up the precursor gases of silane and oxygen to make them more reactive, hence allowing for a lower deposition temperature (≤ 200 °C) compared to chemical vapor deposition (≥ 400 °C). The properties of the deposited silica strongly depend on the ion flux impinging onto the substrate (which can be left “floating” or biased) during the deposition process [4]: low-pressure deposition with ion bombardment leads to amorphous films where the stress needs to be controlled to prevent the film from peeling off in time and to minimize birefringence in the optical device. While deposition above ≥ 400 °C leads to extrinsic stress, which can be reduced by doping to equalize the temperature coefficient of expansion, deposition below 200 °C mostly leads to intrinsic stress resulting from the higher ion flux [5]. We present experimental results on intrinsic compressive stress in films deposited in continuous and pulsed plasmas. The plasma-surface interaction during deposition is investigated by measuring the plasma parameters by energy-selective mass spectrometry and by correlating the results with the measured film stress.

HELICON DEPOSITION REACTOR

The helicon deposition reactor previously described in detail [3] consists of a 15-cm-diameter, 30-cm-long glass tube (the source) surrounded by a helicon antenna and two solenoids, which are contiguous with a 35-cm-diameter, 30-cm-long aluminium diffusion chamber surrounded by two solenoids. For the present results, the magnetic field configuration induces a B_z component of the field of about 80 G in the source and 70 G in the chamber. The reactor (source and chamber attached) is pumped down to a base pressure of about 10^{-5} torr by using a turbomolecular pump placed on top of the source. The silane

*Lecture presented at the 15th International Symposium on Plasma Chemistry, Orléans, France, 9–13 July 2001. Other presentations are presented in this issue, pp. 317–492.

[‡]Also at the Département Sciences Pour l'Ingénieur, CNRS, France.

and oxygen gas inlets are situated on top of the chamber, and total gas flows of 10 to 100 sccm lead to pressures of a few mtorr, measured by a baratron gauge mounted at the back of the chamber. The 4" wafer is placed at the bottom of the chamber. When operating in its resonant regime, this type of reactor produces high plasma densities [6] ($\geq 10^{11}$ cm $^{-3}$ in the chamber). Operating conditions are a radio-frequency power of 800 W and a constant total gas flow of 30 sccm. The main parameter is the oxygen/silane gas flow rate ratio R for continuous mode and the duty cycle for pulsed mode. In pulsed operation, the rf generator/matchbox system has rise and fall times of about 80 and 60 μ s, respectively. The processing chamber is equipped with an *in situ* ellipsometer (632.8 nm) and an energy-selective mass spectrometer (HIDEN $1 \leq \text{a.m.u.} \leq 300$).

RESULTS AND DISCUSSION

In situ measurements

The positive and negative ion spectra and the ion energy distribution function (IEDF) are measured using the mass spectrometer for R ranging from 1 to 10 and for continuous excitation [3]. Typical results are shown in Fig. 1 and Fig. 2 for $R = 10$. The positive ion mass spectrum shows that the main silicon-

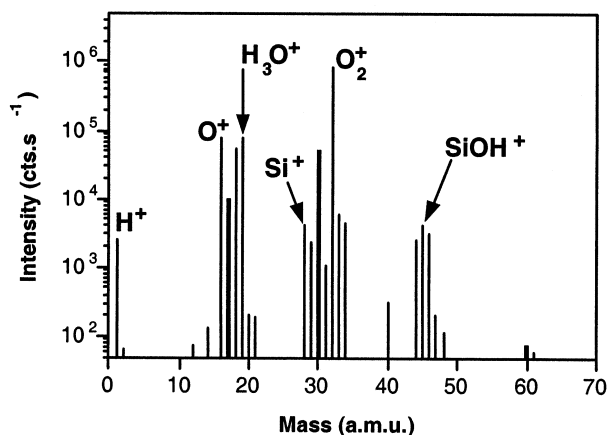


Fig. 1 Positive ion mass spectrum for $R = 10$.

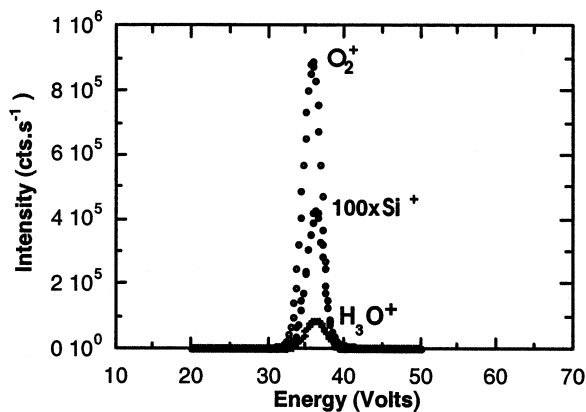


Fig. 2 IEDF of the O_2^+ , H_3O^+ , and Si^+ ions for $R = 10$; for better clarity the Si^+ IEDF has been multiplied by 100.

containing ions are Si⁺ and SiOH⁺ and no polymerization is observed (NO⁺ at mass 30 is a result of the N₂ purge on the pump, a safety requirement). In high-density mode and at low pressure, the silane is fully dissociated and the total positive ion density in the processing chamber is in the 10¹¹ cm⁻³ range. The negative ion mass spectrum shows the presence of O⁻, OH⁻, and H⁻ ions only (no silicon-containing negative ions). Consequently, powder formation generally observed in capacitive systems operating with silane chemistry at high pressure and lower density [7] is not present in the positive ion-rich helicon system for a pure oxygen/silane mixture.

The IEDF of the O₂⁺, Si⁺, and H₃O⁺ ions (Fig. 2) exhibits a single peak around the plasma potential ($V_p \sim 36$ V) which determines the energy [$e(V_p - V_f)$] of the positive ions impinging onto the “electrically floating” ($V_f \sim -10$ V) wafer during the deposition. To calibrate the spectrometer, absolute measurements of the density were performed in a pure oxygen plasma by using a Langmuir probe. The “equivalent ion-induced deposition rate” obtained from the measured fluxes of Si⁺ and SiOH⁺ (the two main ion precursors for the deposition) in Fig. 1 was found to be 50 % of the deposition rate of 25 nm·min⁻¹ measured by the ellipsometer. The positive silicon-containing ions cannot be seen as just an energy source to the wafer but contribute to the silica growth itself.

Ex situ measurements

Additional measurements of the film properties for $R = 10$ showed a refractive index of 1.46, i.e., close to that of a thermal oxide (TO), a stoichiometry of 2, a P-etch of 4 Å·s⁻¹ (2 Å·s⁻¹ for TO) and a Si–O–Si stretching frequency of ~1080 cm⁻¹ (1090 cm⁻¹ for TO of equivalent thickness), the latter suggesting that the silica itself is dense and stressed. Although high ion fluxes generally lead to an improvement in the silica properties (low porosity and low impurity content, such as hydrogen), excessive stress often occurs with the oxides peeling off the substrate, especially when fast deposition of thick films (5 to 20 μm) is required for the waveguide fabrication. Stress results from complex strain mechanisms [8] occurring both at the interface between the substrate and the oxide, and in the bulk of the oxide, a study well beyond the scope of this paper.

It has been shown [9] that compressive stress is dependent on the positive ion energy E and flux j . A common way of varying the ion energy is to bias the substrate during the deposition; for sufficient energy (>hundreds of eV) the stress will eventually decrease, but the other properties of the film might be altered. An alternative solution is to pulse the plasma, thereby somewhat decoupling the role of ions and neutrals [5]. During the pulse, deposition will occur under ions and neutrals and energy will be brought to the surface by the ions. During the post-discharge, deposition will result from the neutral flux with no energy from the ions, a situation similar to the high-pressure, low-density plasma systems [10].

For $R = 3$ and 900 W RF in continuous operation, a large deposition rate of 100 nm·min⁻¹ is obtained, with partial peeling of the layer on the 4” wafer. For pulsed operation, a constant pulse width of 500 μs is used, with a post-discharge varying up to 4.5 ms. This regime allows an adjustment of the time-averaged ion flux. As shown in Fig. 3, the stress could be reduced below the threshold of about 0.3 Gpa, previously found to be the limit for preventing the film from eventually peeling off. For the present conditions, the time-dependence of the stress could be approximated by the following expression:

$$S(t) = \sqrt{E(t)} / [R_o(t) / j(t)]$$

where R_o is the flux of atoms (ions or neutrals) contributing to the growth [5,9]. Consequently, the stress time-constant in the post-discharge will depend on the measured time-constants for R_o , j , and E as shown on Fig. 4. Integrating over the pulsing period leads to the calculation of the expected macroscopic stress [5]. Results are shown on Fig. 3 (solid lines) for two stress time-constants (0 and 80 μs).

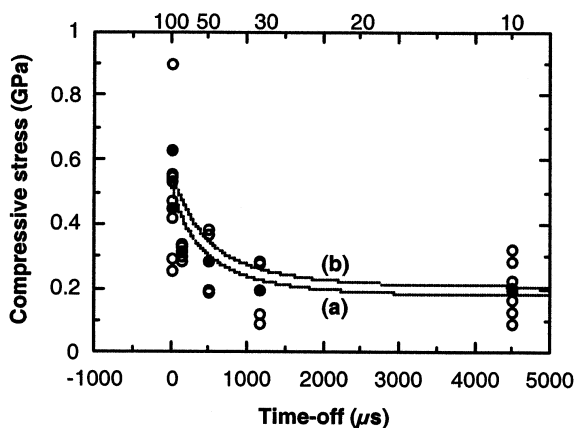


Fig. 3 Measured [\circ] in 4 directions and (\bullet) average] and calculated [solid lines (a) 0 μ s and (b) 80 μ s stress time constant] stress vs. time-off for $R = 3$.

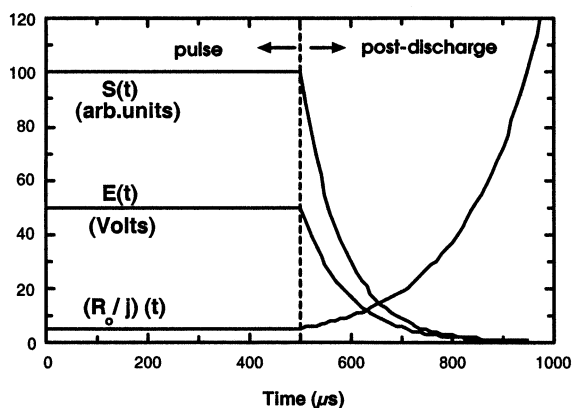


Fig. 4 Time evolution of the plasma parameters and of the calculated stress (pulsed excitation, $R = 3$).

CONCLUSION

In pulsed regimes, a good control of the film stress can be obtained by adjusting the off-time. In these studies, the intrinsic stress model available in the literature [9] has been found to be realistic for plasma deposited films only if j is the flux of ions contributing to the film growth and not the total flux of ions onto the wafer.

REFERENCES

1. M. Kawachi. *Opt. Quant. Elec.* **22**, 391–416 (1990).
2. F. Ladouceur and J. D. Love. *Silica-Based Buried Channel Waveguides and Devices*, Chapman & Hall, London (1996).
3. C. Charles and R.W. Boswell. *J. Appl. Phys.* **81**, 43–49 (1997).

4. O. Joubert, R. Burke, L. Vallier, C. Martinet, R. A. B. Devine. *Appl. Phys. Lett.* **62**, 228–230 (1993).
5. C. Charles and R.W. Boswell. *J. Appl. Phys.* **84**, 350–354 (1998).
6. R. W. Boswell and F. Chen. *IEEE Trans. Plasma Sci.* **25**, 1229–1244 (1997).
7. A. A. Howling, J. L. Dorier, C. Hollenstein. *Appl. Phys. Lett.* **62**, 1341–1343 (1993).
8. S. M. Hu. *J. Appl. Phys.* **70**, R53–R80 (1991).
9. C. A. Davis. *Thin Solid Films* **226**, 30–34 (1993).
10. M. A. Lieberman and A. J. Lichtenberg. *Principles of Plasma Discharges and Materials Processing*, Wiley, New York (1994).