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Enhanced tunability of the composition in silicon oxynitride thin films by the reactive gas pulsing process

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ABSTRACT

Silicon oxynitride thin films were sputter deposited by the reactive gas pulsing process. Pure silicon target was sputtered in Ar, N_2 and O_2 mixture atmosphere. Oxygen gas was periodically and solely introduced using exponential signals. In order to vary the injected O_2 quantity in the deposition chamber during one pulse at constant injection time (T_{ON}), the tau mounting time τ_{mou} of the exponential signals was systematically changed for each deposition. Taking into account the real-time measurements of the discharge voltage and the $I(O^*)/I(Ar^*)$ emission lines ratio, it is shown that the oscillations of the discharge voltage during the T_{ON} and T_{OFF} times (injection of O_2 stopped) are attributed to the preferential adsorption of the oxygen compared to that of the nitrogen. The sputtering mode alternates from a fully nitrided mode (T_{OFF} time) to a mixed mode (nitrided and oxidized mode) during the T_{ON} time. For the highest injected O_2 quantities, the mixed mode tends toward a fully oxidized mode due to an increase of the trapped oxygen on the target. The oxygen (nitrogen) concentration in the SiO_xN_y films similarly (inversely) varies as the oxygen is trapped. Moreover, measurements of the contamination speed of the Si target surface are connected to different behaviors of the process. At low injected O_2 quantities, the nitrided mode predominates over the oxidized one during the T_{ON} time. It leads to the formation of $Si_3N_{4-y}O_y$-like films. Inversely, the mixed mode takes place for high injected O_2 quantities and the oxidized mode prevails against the nitrided one producing $SiO_{2-x}N_x$-like films.

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1. Introduction

Silicon-based compounds such as silicon oxynitrides have been and are still subject to intensive investigations because their versatile properties can lead to various applications fields, e.g. in integrated circuits due to the high dielectric constant [1–7], in optoelectronics as optical waveguides [8] or antireflection coatings [9,10] due to the tunable refractive index, but also in micro electro mechanical systems (MEMS) [11,12]. Furthermore, these compounds exhibit good scratch resistance [13], thermal stability [14], chemical inertness [15] and low impurity diffusion [16]. They are largely used as passivation layer in microelectronics and optoelectronics [17–19], and consequently the applications have been extended to gaseous diffusion barriers [20,21]. The main interest of silicon oxynitrides is in the faculty to tailor intermediate properties from silicon nitride to silicon oxide as a function of the metalloid amount. They have especially been synthesized by PVD [22–24] or PECVD methods [25]. Nevertheless in chemical processes, their properties can chiefly be deteriorated due to significant hydrogen concentrations coming from the decomposition of the gaseous precursors [26–28]. As a result, physical processes and particularly reactive sputtering is an attractive way to reach SiO_xN_y thin films with adjustable oxygen and nitrogen contents. As previously reported in numerous works [29–35], the reactive sputtering process often exhibits non linear behaviors as a function of the reactive gas flow rate. It becomes even trickier when two reactive gases like O_2 and N_2 are simultaneously injected into the process [36,37]. Since oxygen exhibits a stronger reactivity than nitrogen with regards to silicon, a constant introduction of O_2 and N_2 limits the range of achievable metalloid concentrations in the films and does not solve the drawbacks of the reactive sputtering mode. Some original approaches were proposed by Sproul et al. [38,39] by means of a feedback control system of the reactive gases using mass spectrometry. Recently, Aubry et al. [40] successfully applied the reactive gas pulsing process (RGPP) to synthesize silicon oxynitride films with an adjustable O/N ratio in the as-deposited films. This RGPP approach has also been successfully applied to other oxynitride films sputter deposited by reactive sputtering [41–47].

In this article, we aim at showing the possibility to improve the accuracy for the adjustment of the metalloids chemical

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composition. In order to achieve this objective, silicon oxynitride thin films were deposited by reactive magnetron sputtering from Si target by pulsing the oxygen gas. The influence of the O_2 quantities introduced using a rectangular pulsing signal has previously been reported [48]. We have demonstrated that the synthesis of SiO_xN_y films with tunable x and y coefficients is only achieved for a given range of injected O_2 quantities (lower than 12 Pa L), which limits the composition variations. In this study, such a range of injected O_2 quantities (in-between 0 and 12 Pa L) has been more accurately controlled by means of exponential pulses. Varying some temporal parameters of the exponential shape (e.g. the tau mounting time τ_{mou}), a narrow sampling of the metalloids content was successfully completed leading to the formation of two kinds of films: $Si_3N_{4-y}O_y$ and $SiO_{2-x}N_x$-like compounds.

2. Materials and methods

A stainless-steel vacuum reactor (40 L) was evacuated by a turbo molecular pump assisted by a mechanical pump leading to a base pressure of 10^{-5} Pa. The average pumping speed and the target-to-substrate distance were set at 12.3 L s^{-1} and 50 mm, respectively. The Si target (purity 99.99 at.% and 2 inch diameter) was DC sputtered using a constant current density of 49 A m^{-2}. Silicon oxynitride thin films were prepared on grounded silicon substrates at room temperature in Ar + O_2 + N_2 gas mixture. The Ar and N_2 gases were first introduced into the chamber with continuous flow rates of 4 and 3 sccm, respectively. The N_2 flow rate was high enough to sputter the target in the nitrided mode in Ar + N_2 atmosphere. In addition, in Ar + O_2 atmosphere, it was preliminary verified that using a constant O_2 flow rate of 1.2 sccm ensured an oxidized sputtering mode of the Si target. The O_2 gas was periodically injected in the chamber following exponential pulses with minimal and maximal flow rates of 0 and 1.2 sccm, respectively. Exponential signals versus time and associated parameters were defined according to two independent equations [41]. During the T_{ON} time, the setpoint of the oxygen flow rate $Q\,O_2(t)$ versus time t can be described by the following equation:

$$Q\ O_2(t) = (Q\,O_{2\mathrm{Max}} - Q\,O_{2\mathrm{Min}}) \times \frac{1-\exp^{-t/\tau_{mou}}}{1-\exp^{-T_{ON}/\tau_{mou}}} + Q\ O_{2\mathrm{Min}} \quad (1)$$

where $Q\,O_{2\mathrm{Max}}$ is the maximum oxygen flow rate (sccm), $Q\,O_{2\mathrm{Min}}$ is the minimum oxygen flow rate (sccm) and τ_{mou} is the tau mounting time (s). Similarly and during the T_{OFF} time, the equation is:

$$Q\ O_2(t) = (Q\,O_{2\mathrm{Max}} - Q\,O_{2\mathrm{Min}}) \times \left(1-\frac{1-\exp^{-t/\tau_{des}}}{1-\exp^{-T_{OFF}/\tau_{des}}}\right) + Q\ O_{2\mathrm{Min}} \quad (2)$$

where τ_{des} is the tau descending time (s). Therefore, various shapes of the oxygen injection flow rate can theoretically be generated (Fig. 1a). Keeping $\tau_{des} = 10^{-1}$ s and $Q\,O_{2\mathrm{Min}} = 0$ sccm (which corresponds to no injection of O_2 during the T_{OFF} time), a Dirac-like peak is created for the lowest and negative values of the tau mounting time ($-1.5 \le \tau_{mou} < -10^{-3}$ s), the signal becomes a triangle as τ_{mou} tends to the minus infinite ($-60.0 \le \tau_{mou} < -1.5$ s) and finally a rectangle for the lowest and positive τ_{mou} values ($+10^{-3} \le \tau_{mou} \le +1.75$ s).

In this study, the pulsing period T and the oxygen injection time T_{ON} were kept at 20 and 6 s, respectively. So, the resulting duty cycle α defined by the ratio T_{ON}/T was fixed at 0.3. The oxygen supply was stopped during the T_{OFF} time, i.e. $\tau_{des} = 10^{-1}$ s and $Q\,O_{2\mathrm{Min}} = 0$ sccm. In order to vary the injected O_2 quantity during the T_{ON} time, the tau mounting time τ_{mou} was systematically modified. For all films, the deposition time was 120 min leading to a thickness close to 700 nm for any operating conditions. As a result, the deposition rate was in the range 5.2–6.2 nm min^{-1}. Taking into account these experimental data, one can assume that neither periodic multilayered nor nanocomposite structures can be produced. During a pulsing period T = 20 s, T_{ON} = 6 s and T_{OFF} = 14 s, which correspond to a calculated thickness of 5–6 Å and 12–14 Å, respectively. In addition, these thicknesses are certainly overestimated due to the pulse shape (more progressive oxidation/nitridation contrary to the rectangular pulse). For this thickness range and due to the diffusion phenomena during the growing film, mixing of metalloid and silicon elements certainly occurs, which prevent the deposition of a multilayered architecture. In addition, the formation of a nanocomposite structure (nanosized particles into a matrix) can be ruled out due to the amorphous structure systematically observed.

The light emitted by discharge was recorded in real time by optical emission spectrometry with a Ocean optics HR 4000 spectrometer connected to UV–VIS–NIR optical fiber located in front of the target. The fiber was protected from contaminations during the deposition by a stainless steel pipe. The spectral resolution was lower than 1 nm. The chemical composition of the as-deposited films on Si substrates was determined by secondary neutral mass spectrometry (SNMS), consisting in a secondary ion mass spectrometer (VG Simslab instrument) equipped with a thermionic filament. A 500 × 500 μm^2 surface was analyzed by Ar^+ primary ion beam. The elementary composition of SiO_xN_y films was calculated from the relative ionization rates of O and N elements to Si in SiO_2 and Si_3N_4 films, assuming as a constant the relative ionization rate with respect to the different chemical environments. The $14N^{2+}$ signal (7 a.m.u.) was carefully taken into account so as to avoid an overestimation of the nitrogen content in the films.

3. Results and discussion

3.1. Discharge behaviors

From real time measurements of the oxygen flow rate versus time, it can be observed that the experimental signals (output) of the flow rate do not strictly correspond to the theoretical setpoints given by Eqs. (1) and (2) (Fig. 1b). This discrepancy is ascribed to the delay time and to the increment accuracy of the gas flowmeter. As a result, the injected O_2 quantity, namely *IOQ*, truly supplied into the deposition chamber during one period has been calculated from integration of the O_2 flow rate signals versus time [40]. These

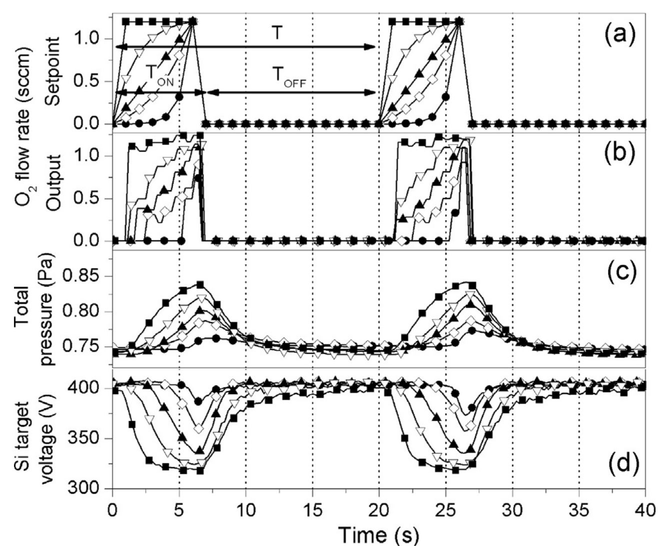

Fig. 1. Setpoint (a) and output (b) O_2 flow rates as a function of time for various tau mounting times τ_{mou}. Temporal evolution of the resulting (c) total pressure and (d) Si target voltage. The corresponding injected O_2 quantities are indicated in parenthesis. (■) $\tau_{mou} = +10^{-3}$ s (*IOQ* = 11.7 Pa L), (▽) $\tau_{mou} = +1.75$ s (*IOQ* = 8.5 Pa L), (▲) $\tau_{mou} = -60.0$ s (*IOQ* = 5.4 Pa L), (◇) $\tau_{mou} = -3.0$ s (*IOQ* = 3.7 Pa L), (●) $\tau_{mou} = -0.75$ s (*IOQ* = 1.0 Pa L). The tau descending time τ_{des} was maintained constant at 0.1 s.

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