Thin Solid Films 642 (2017) 281–284

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Characteristics of silicon oxynitride films grown by using neutral-beams and inductively coupled plasma

Jongsik Kim*, Dae Chul Kim, Young-Woo Kim

Core Technology Research Division, Plasma Technology Research Center, National Fusion Research Institute, Daejeon 34133, Republic of Korea

ARTICLE INFO

Keywords:
Silicon oxynitride
Neutral beam
Plasma-enhanced chemical vapor deposition
Room temperature deposition
Plasma damage
Electrical properties
Secondary ion mass spectrometry

ABSTRACT

The characteristics of silicon oxynitride (SiON) films grown using neutral-beam and typical plasma-enhanced chemical vapor deposition methods are compared. Neutral-beam and plasma oxynitridation processes were performed using a nitrogen neutral beam at room temperature and a nitrogen plasma at 400 °C, respectively, using the same deposition system. The neutral beam was generated via the surface neutralization of the ions produced by the inductively coupled plasma. The physical and electrical properties were measured using metal-insulator-silicon structures. The plasma SiON films showed significant plasma-induced damage, while we demonstrate that the neutral beam method is suitable for growing SiON films at room temperature without plasma-induced damage or a high thermal budget.

1. Introduction

Plasma is one of the most widely used tools in the processing of semiconductor and display materials as it can provide the required energy and active radicals for low-temperature etching, ashing, and thin film deposition. However, as the integration of silicon wafers reaches the nano-level, plasma-induced damage and ion interaction issues are becoming major obstacles for technological advances in etching and related processes [1–5]. For example, state-of-the-art etching of very small structures must resolve challenges arising from charge interactions, such as undercuts and the loading effect. In addition, the emerging large-area flat panel industry desires solutions for problem caused by plasma charging due to the dielectric nature of the glass substrates [6]. Many approaches have been explored to avoid the fundamental challenges of plasma-based methods. A promising clean alternative solution is the energetic neutral beam [7], which when applied with the appropriate energy prevents charge interactions and plasma-induced damage [8].

Silicon oxynitride (SiON) films that are formed by incorporating nitrogen atoms into SiO_2 films are proposed as gate insulators because of their reduced direct tunneling and improved device reliability [9]. SiON films are used in important applications including protective layers and insulators in optical devices, such as optical communication waveguides [10]; in flexible devices, such as for thin film encapsulation of unconventional substrates (i.e., plastics) [11]; and for gate dielectrics [12]. Conventionally, SiON films are grown on silicon substrates at $>$ 800 °C by thermal or rapid thermal annealing oxynitridation in nitrogen or ammonium environments [10] and plasma-enhanced chemical vapor deposition (PECVD) in NO or N_2O gas [13–14]. In the cases of thermal and rapid thermal annealing (RTA) oxynitridation techniques, the nitrogen content in the film is usually $<$ 10% and the nitrogen is mainly concentrated around the gate oxide/Si substrate interface, which causes negative bias temperature instability [15]. It follows that annealing either in a furnace or an RTA reactor may influence the stability and electro-physical properties of the gate dielectric layers. Hence, to fabricate suitable ultra-thin dielectric layers for complementary metal-oxide semiconductor technologies, a low-temperature process is important to reduce the thermal budget for device manufacturing [16]. The PECVD approach is advantageous in some cases as it enables good control of the chemical composition by varying the deposition parameters [17]. Recent PECVD studies, aiming to utilize these films in optical waveguides and metal oxide semiconductor devices, have reported good control of the dielectric constant by modifying the deposition conditions [18]. Alternatively, many approaches have been explored to avoid inherent plasma-induced defects, where the most favorable solution is an energetic neutral beam [7]. Neutral beams with the appropriate energy fundamentally avoid any charge interactions and plasma-induced damage [8].

In this study, we compare the characteristics of SiON films grown by the neutral beam and PECVD techniques. The neutral beam SiON films were grown at room temperature and the plasma SiON films were grown at 400 °C. We demonstrate that the neutral beam method avoided plasma-induced damage and has potential applications for fabricating thin films. The neutral beam was generated through a

---

* Corresponding author.
E-mail address: jongsik@nfri.re.kr (J. Kim).

http://dx.doi.org/10.1016/j.tsf.2017.09.024
Received 23 May 2017; Received in revised form 6 September 2017; Accepted 12 September 2017

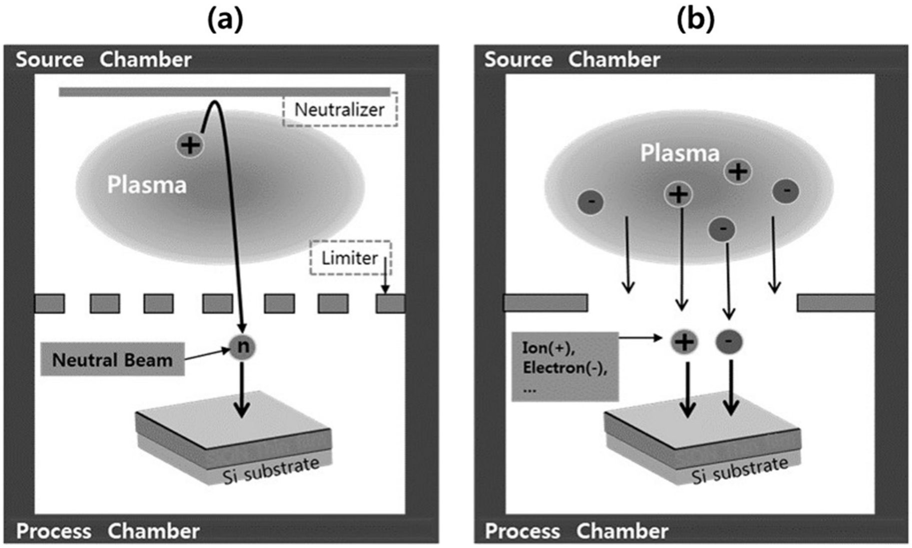

Fig. 1. Schematic diagram showing the (a) neutral beam source and (b) plasma source.

surface neutralization process; a neutralization plate was installed at the plasma boundary, which was biased to extract ions with the appropriate energy from the plasma [19–20]. We report the properties of the SiON films and compare the effects of processing using a neutral beam or plasma. The refractive indices of SiON films were measured by ellipsometry. Capacitance-voltage (C-V) and current-voltage (I-V) measurements were performed to evaluate the insulator-semiconductor interface and bulk properties. The nitrogen depth profiles were measured by secondary-ion mass spectrometry (SIMS).

2. Experimental details

The neutral beam was a neutral stream with particle energies between 1 and 100 eV [19]. The neutral beam source consisted of an inductively coupled plasma (ICP) source, a neutralization plate (usually called a reflector), and a limiter, as shown in Fig. 1(a) [21]. Neutral beam generation depends on the principle of Auger surface neutralization. When ICP-generated charged particles travel through the reflector, they are converted into an energetic neutral beam by capturing electrons from the reflector surface. The reflector material was tungsten to generate a high-flux nitrogen neutral beam. To control the energy of the ions impinging on the reflector, the reflector was electrically isolated using an insulator and was biased at − 20 V. The limiter consisted of an array of permanent magnets to prevent charged particles from flowing down onto the substrate. The neutral beam energy was measured by a neutral particle energy analyzer, which consisted of an ionization cell and ion energy analyzer [19].

Plasma oxynitridation was performed inside a plasma chamber as for the typical plasma processing, as shown in Fig. 1(b). In this case, only an ICP source was used, without a neutralization plate and limiter. The same plasma source and process chamber were used for both the neutral beam and plasma oxynitridation experiments. The oxynitridation source for both the neutral beam and plasma processes was the internal ICP nitrogen plasma. To grow the SiON films, N_2 gas (99.999%) was fed into the ICP source chamber. The substrates sat on a stainless steel electrode and the temperature of the electrode was controlled by a heater. The growth parameters used to fabricate the SiON films in this work are listed in Table 1.

The SiON films made using the neutral beam and plasma methods were grown on thermally oxidized SiO_2 films. A p-type 〈100〉 silicon wafer with a resistivity of about 0.001–0.005 Ω·cm was used as the substrate. The wafer was first cleaned using the standard RCA clean method and then the natural oxide film was removed by etching in diluted 10% HF (48%) solution. A thermal SiO_2 film with an average thickness of 54 Å was then grown in a furnace reactor at 800 °C. To grow SiON films, the SiO_2 wafers were exposed to the nitrogen neutral beam at room temperature or the nitrogen plasma at 400 °C.

Table 1
Deposition conditions for neutral beam SiON and plasma SiON films.

	Neutral beam SiON			Plasma SiON		
RF input power (13.56 MHz) (W)	1500			1500		
Operating pressure (mTorr)	1.0			1.0		
N_2 flow rate (sccm)	10			10		
Base pressure (Torr)	$< 2.0 \times 10^{-6}$			$< 2.0 \times 10^{-6}$		
Substrate temperature (°C)	25 (Room temperature)			400		
Process time (min)	1	5	10	1	5	10
Thickness (nm)	5.5	9.8	14.5	5.7	14.3	21.2

For electrical measurements, metal insulator semiconductor (MIS) structures were produced. The metal gates of the MIS capacitors were formed post-oxidation from aluminum. Al gates with diameters of 160 μm were deposited by thermal evaporation using a shadow mask to define the gate areas. The natural oxide on the back side of each SiON sample was removed with a diluted 10% HF (48%) solution, followed by the evaporation of an Al layer to form an Ohmic contact for these structures. Then, post-metal annealing at 400 °C was undertaken for 30 min in N_2 gas. The thickness and refractive indices of the SiON films were measured by ellipsometry (J.A. Woollam, V-VASE) with a wavelength of 635 nm. The capacitance values and leakage currents were obtained by C-V and I-V measurements, respectively (Keithley, 4200-SCS). High-frequency (i.e., 1 MHz) C-V measurements were performed with a sweep rate of 100 mV/s; the voltage was swept from a positive to a negative gate bias and back. The nitrogen depth profile was measured using SIMS. A CAMECA IMS-6f magnetic sector SIMS instrument was used in the SIMS measurements. A beam of 1 keV Cs^+ ions of ~3 nA was incident on the SiON films. The ion signal of $^{133}Cs^{14}N^+$ was detected for depth profiling of nitrogen, respectively.

3. Results and discussion

Before characterizing the SiON films, we measured the plasma parameters using a Langmuir probe. The electron density was about 1×10^{11} #/cm^3 and the electron temperature was about 3–4 eV. Fig. 2 shows the measured neutral beam energies, which increased as the reflector voltage increased. The measured peak energies of the neutral beam were about 40% of the reflector bias voltage. The first peak relates to the distribution of plasma ions. The neutral beam energy