Stress control of silicon nitride films deposited by plasma enhanced chemical vapor deposition*

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Stress controllable silicon nitride (SiN_x) films deposited by plasma enhanced chemical vapor deposition (PECVD) are reported. Low stress SiN_x films were deposited in both high frequency (HF) mode and dual frequency (HF/LF) mode. By optimizing process parameters, stress free (−0.27 MPa) SiN_x films were obtained with the deposition rate of 45.5 nm/min and the refractive index of 2.06. Furthermore, at HF/LF mode, the stress is significantly influenced by LF ratio and LF power, and can be controlled to be 10 MPa with the LF ratio of 17% and LF power of 150 W. However, LF power has a little effect on the deposition rate due to the interaction between HF power and LF power. The deposited SiN_x films have good mechanical and optical properties, low deposition temperature and controllable stress, and can be widely used in integrated circuit (IC), micro-electro-mechanical systems (MEMS) and bio-MEMS.

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Silicon nitride (SiN_x) can be used as diffusion barriers for mobile ions, passivation layers for electronic and optoelectronic devices or a gate insulator in field effect transistors[1,2]. It is also used as optical coatings for solar cells[3,4] or biomaterial for deoxyribonucleic acid (DNA) and protein microarray[5]. Recently, the applications of SiN_x films have been extended to silicon photonics[6] and lithium ion battery[7].

There are many deposition methods for SiN_x films, such as low pressure chemical vapor deposition (LPCVD), plasma enhanced chemical vapor deposition (PECVD)[8], and high density plasma enhanced chemical vapor deposition techniques using electron cyclotron resonance plasma (ECR-PECVD)[9] or inductively coupled plasma (ICP-PECVD)[10]. Among them, PECVD is attractive due to the low deposition temperature, high deposition rate and good film uniformity. Generally, a low stress SiN_x film has wide applications, such as the diaphragm in film bulk acoustic-wave resonator (FBAR) devices, three-dimensional (3D) passivation layer for sensors, and suspensions in micromachined silicon accelerometers[11]. However, for some special applications, a large stress is required[12]. So the methods of controlling residual stress in SiN_x layers to a desired value are needed.

This paper aims at an effective stress control of SiN_x layers with good mechanical and optical properties deposited by PECVD. Both high frequency (HF) mode and dual frequency (HF/LF) mode are studied. The effects of main process parameters in the fabrication of the SiN_x layers, such as radio frequency (RF) power, pressure, SiH_4 and NH_3 flow rates, LF/HF ratio, are presented. Special attention is paid to the stress control methods of SiN_x layers. Finally, repeatability of low stress SiN_x film deposition process is also examined.

The deposition processes were achieved in the PECVD system of FHR-PECVD 100, which is a coupled planar parallel electrode system. The system was equipped with an HF generator at 13.56 MHz with a maximum power of 300 W and an LF generator at 300 kHz with a maximum power of 600 W. The base pressure for pre-deposition was 1×10^{-3} Pa. In order to obtain the exact temperature on the substrate in process mode, the thermocouple was placed on the substrate, and the temperatures both on the heater and on the substrate were achieved as shown in Fig.1, whose chamber pressure was set to be 40 Pa. The thickness and refractive index were measured by an ellipsometer of Auto EL-AV. The stress of the film was obtained by the stress meas-

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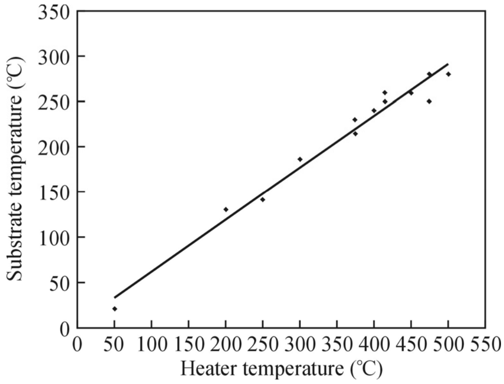

Fig.1 Relationship between the temperatures on the substrate and on the heater

For all experiments, double-side polished, n-type and <100>-oriented single-crystalline silicon wafers with the diameter of 10.16 cm and the thickness of 500±25 μm were used as substrates. Prior to the thin film deposition, the substrates were chemically cleaned by a piranha solution (a mixture of concentrated H_2SO_4 and 30% H_2O_2 with a volume ratio of 3:1) at 80 °C for 10 min, and then were submerged in buffered hydrofluoric acid to remove the native oxide from the wafer surface. When the substrate was loaded in the reaction chamber, it was baked for 20 min in the argon atmosphere to ensure temperature uniformity. The side wall of the chamber was heated up to 50 °C in order to prevent the SiN_x depositing on the sidewall. The deposition temperature (heater temperature) was varied from 200 °C to 300 °C with the substrate temperature from 130 °C to 190 °C. Both HF mode and HF/LF mode with different time intervals were applied. The 25% silane (SiH_4, diluted by helium) and undiluted ammonia gas (NH_3) were used as the precursor gases. The SiH_4 flow rate was set to be 80 cm^3/min and kept constant, and the NH_3 flow rate was varied from 60 cm^3/min to 200 cm^3/min. The chamber pressure was adjusted from 100 Pa to 200 Pa by a throttle valve. For safety reason, the chamber and the gasline must be purged with argon for more than 5 circles before getting the wafer out.

High frequency RF mode is the most common operation mode in the PECVD system. Firstly, the SiN_x films were deposited at HF mode. The deposition power was changed from 40 W to 200 W, while the heater temperature and pressure were set to be 300 °C and 100 Pa, respectively. Fig.2 shows the variations of the residual stress and deposition rate of SiN_x films respectively with the HF power. It can be observed that at HF mode, the SiN_x layers exhibit compressive stress in the range from −80 MPa to −600 MPa. The compressive stress increases with the increase of RF power, while the deposition rate changes strongly when RF power increases from 40 W (around 12 nm/min) to 100 W (around 45 nm/min), and changes slightly when RF power increases from 100 W to 200 W. The increased RF power leads to a higher electron density, which yields a higher dissociation rate of reactant gases, then the deposition rate increases. However, when RF power increases to 100 W, the dissociation of gases reaches the saturation state, so the deposition rate increases slightly. The high compressive stress is attributed to the ion bombardment caused by high electron energy, which causes the extrusion between neighboring molecules. However, the stress of SiN_x layers is always compressive, not tensile, which is different from the results mentioned in other articles[13,14]. This is due to the low chamber pressure.

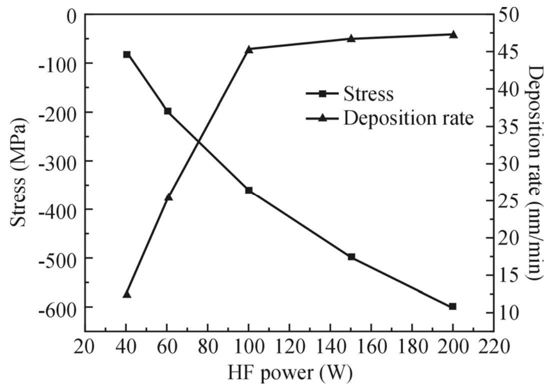

Fig.2 Variations of stress and deposition rate of the SiN_x layers with HF power

The pressure in a vacuum chamber is usually used to ensure a stable glow discharge[15], and can greatly influence the characteristics of SiN_x layers. Fig.3 shows the residual stress and the deposition rate with change of chamber pressure. It indicates that pressure has a great effect on the SiN_x deposition rate and stress. The deposition rate firstly increases with the increase of pressure, and then reaches the maximum of 45.9 nm/min at pressure of 150 Pa. As the pressure increases from 150 Pa to 200 Pa, the deposition rate changes slightly. The reason is that as increasing the chamber pressure, the concentration of the reactant gas gets higher, which leads to accelerating the reaction process and increasing the deposition rate. But at higher chamber pressure, the ion collision increases, and the electron energy reduces. At this point, a balance between the film deposition and the gas dissolution is achieved, resulting in slight changes of deposition rate. Furthermore, the stress of SiN_x layers changes from compressive to tensile as the pressure increases. This is due to the low pressure increases the electron energy, which makes more N_2 active while more N-H bonding, namely the Si/N ratio is decreased.

Moreover, the refractive index and uniformity of SiN_x layers are also analyzed, as shown in Fig.4. It can be seen that the refractive index and uniformity change randomly with pressure. This may be attributed to the non-stabilization of plasma caused by pressure. It is worth noting that the SiN_x layers at a pressure of 160 Pa result in the refractive index of 2.06 and the uniformity of ±0.8%.

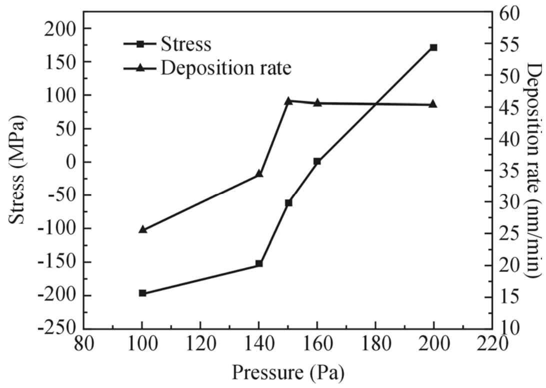

Fig.3 Variations of stress and deposition rate of the SiN_x films with pressure

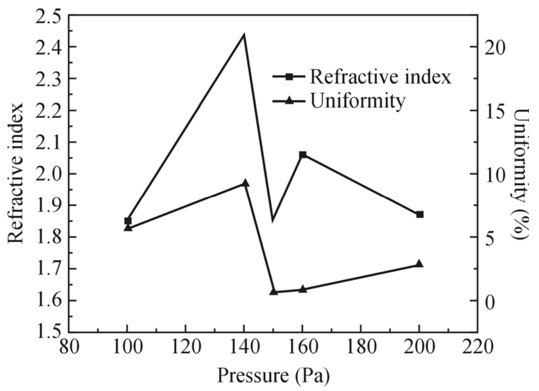

Fig.4 Variations of refractive index and uniformity of the SiN_x layers with pressure

It can be concluded from the above analyses that the pressure around 160 Pa is optimum for SiN_x deposition due to its stable plasma and low residual stress. The repetitive experiments for five times were carried out with the same process parameters. The results are shown in Tab.1, which indicates that the low stress SiN_x layers have good conformity for stress, thickness, refractive index and uniformity.

Tab.1 Repetitive experimental results for low stress SiN_x layers

Number	Stress (MPa)	Deposition rate (nm/min)	Refractive index	Uniformity (%)
1	−7.8	44.6	2.132	±1.27
2	−15.8	45.1	2.132	±0.96
3	−0.27	45.5	2.063	±0.84
4	−15.7	45.6	2.059	±1.45
5	−13.1	45.4	2.078	±0.65
Average	−10.5	45.2	2.093	±1.034

Among all process parameters, NH_3 flow rate has the most important influence on the refractive index of SiN_x layers. Furthermore, it has great effect on stress and deposition rate due to its influence on the composition of SiN_x layers. In our experiments, the NH_3 flow ratio is varied from 60 cm^3/min to 200 cm^3/min. The heater temperature is set to be 300 °C, and the pressure is 160 Pa. The stress and deposition rate with the increase of NH_3 flow rate are shown in Fig.5. It can be seen that the residual stress is increased and deposition rate is decreased as the NH_3 flow rate increases. The high NH_3 flow rate leads to generating more N+ species, and the incorporation of N bonding is increased in the SiN_x layers, namely the N-rich SiN_x layers. This results in tensile stress due to the volume expansion of the SiN_x layers. The decrease of the deposition rate with increasing NH_3 flow rate can be explained by the decreasing number of Si species in the plasma that generates a decrease in the film growth of precursor $Si(NH_2)_3$[16].

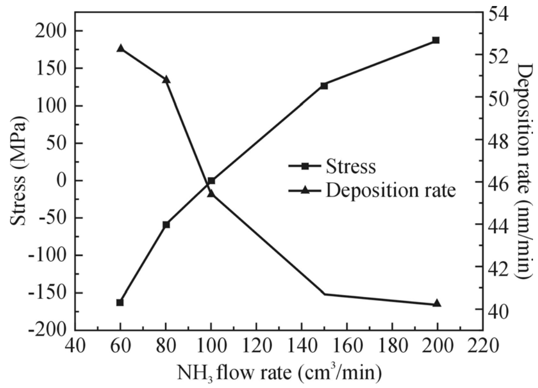

Fig.5 Variations of stress and deposition rate of the SiN_x layers with NH_3 flow rate

The relationship between refractive index and NH_3 flow rate is also studied, as shown in Fig.6. It is obvious that at lower NH_3 flow rate, the refractive index decreases rapidly with the increase of NH_3 flow rate. However, when NH_3 flow rate is greater than 100 cm^3/min, the refractive index decreases slowly and almost keeps constant. That is because as the NH_3 flow rate increases, the SiN_x layer changes from Si-rich state to N-rich state and results in the decrease of film density. This phenomenon indicates that the change of refractive index in Si-rich film is faster than that in N-rich film. Because for Si-rich film, Si-Si bonds lead to the quick changes of film structure and components, while for

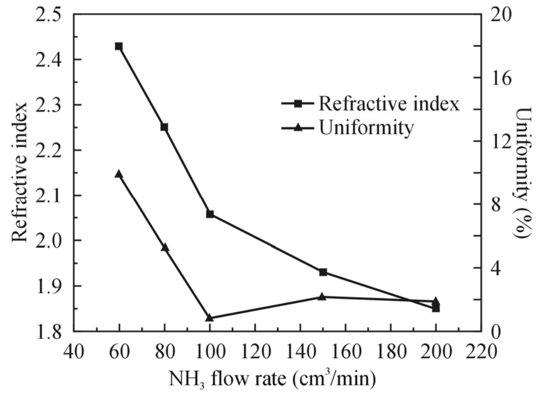

Fig.6 Effect of NH_3 flow rate on refractive index and uniformity

N-rich film, the superfluous N atoms can form some other molecules, such as NH_3, and go away from the surface. Another interesting aspect is that the NH_3 flow rate presents a strong effect on the uniformity of SiN_x layer. For a high NH_3 flow rate (100—200 cm^3/min), the achieved uniformity is better than ±3%, while for a low NH_3 flow rate (60 cm^3/min), the uniformity is between ±5% and ±10%.

Deposition temperature also has a great impact on the stress of SiN_x layers, as shown in Fig.7. It is noted that the stress of SiN_x layers increases with the increase of deposition temperature. On the one hand, it is mainly due to the difference of linear thermal expansion coefficients (LTECs) between SiN_x layer and the Si substrate. LTEC of SiN_x deposited at 20 °C is 3.67×10^{-6} °C^{-1}, while it becomes 4.33×10^{-6} °C^{-1} when it is deposited at 300 °C[17]. On the other hand, as the deposition temperature increases, more reactive ions are deposited on the substrate, and the ions don't have enough time to arrange orderly, which results in a loose film. SiN_x layers deposited at 300 °C are almost stress-free despite the difference in LTEC. This proves that the residual stress in SiN_x layers is not only caused by the difference of LTECs between SiN_x layers and Si substrate but also related with PECVD process parameters which determine the film composition, structure and other properties.

As mentioned above, although stress-free SiN_x layer can be deposited at HF mode, it yields more tensile residual stress as the pressure is higher than 200 Pa, and it is hardly to be lower down. The low frequency generates compressive stress due to the high ion bombardment, so low stress SiN_x layers can be deposited by stacking a sequence of tensile and compressive layers, which means applying HF power and LF power alternatively during the deposition process. The working principle of HF/LF mode is shown in Fig.8. For continuous and stable plasma and high density reaction particles, the HF power is set to be 60 W in the whole deposition process. The deposition time of HF power is t, and it is divided into several circles. Each circle contains the deposition time t_2 and the time intervals t_1. So the LF ratio is defined as $t_2/(t_1+t_2)$.

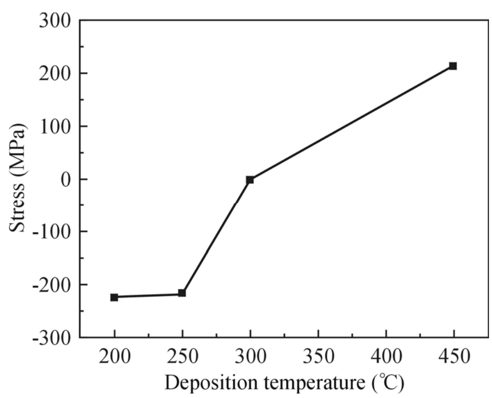

Fig.7 Stress of SiN_x layers as a function of deposition temperature

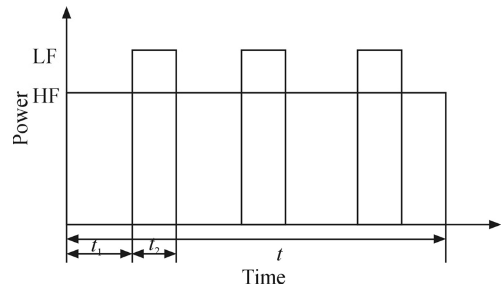

Fig.8 Working principle of HF/LF mode

Fig.9 illustrates the stress variation with the LF ratio in total power. The SiN_x layers were deposited at 300 °C using LF power of 150 W and pressure of 200 Pa. It can be found that the LF ratio of 17%—22% can result in low stress SiN_x layer. High LF ratio results in high compressive stress, confirming that the intrinsic stress of SiN_x layers deposited at LF mode is compressive. The main reason is that at LF mode, the ion bombardment is significantly higher[18], which not only enhances the chemical reactions but also causes a low energy ion implantation that densifies the film and leads to the compressive stress. However, it is noted that the compressive stress does not always increase with the increase of LF ratio. When the LF ratio is lower than 6%, the compressive stress declines seriously with the increase of LF ratio. On one hand, at low LF ratio, the ions can't deposit on the substrate in such a short time although there are more ion bombardments in the chamber, so the HF power plays a leading role. On the other hand, the ion bombardments weaken the electron density and energy, resulting in the decrease of compressive stress. The longer the LF time, the lower the compressive stress.

Fig.10 shows the stress and deposition rate of SiN_x layers deposited at HF/LF mode with different LF powers between 15 W and 150 W. It is noted that LF plasma enhances the compressive stress of SiN_x films, and the compressive stress decreases with the increase of LF power due to the increase of ion bombardments. However, it also can be seen that the LF power has a little effect on the deposition rate. The deposition rate changes from 45.4 nm/min to 46.8 nm/min as the LF power varies from 15 W to 150 W. That is due to the interaction between ion bombardments and electron energy in HF/LF mode.

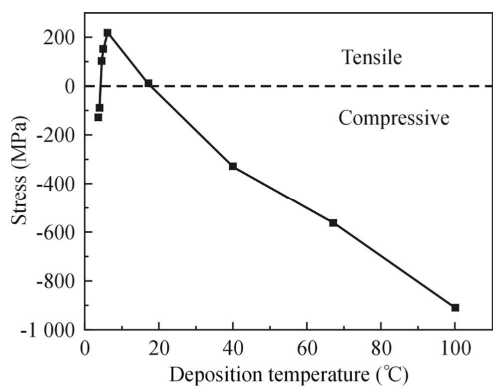

Fig.9 Stresses of SiN_x layers at different LF ratios

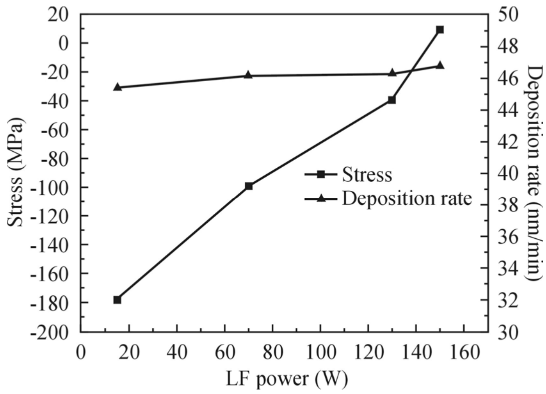

Fig.10 Variations of stress and deposition rate of the SiN_x layers deposited at HF/LF mode with LF power

Knowing the influence of process parameters on the residual stress of SiN_x layers, the stress of SiN_x layers can be controlled in a large range and can be used for different applications. Here, the optimal deposition process parameters for low stress SiN_x layers are listed in Tab.2.

Tab.2 Optimal deposition process parameters for low stress SiN_x films

Modes	Parameters	
HF mode	HF power (W)	60
	SiH_4 flow rate (cm^3/min)	80
	NH_3 flow rate (cm^3/min)	100
	Pressure (Pa)	160
	Deposition temperature (°C)	300
HF/LF mode	HF/LF power (W)	60/140
	SiH_4 flow rate (cm^3/min)	80
	NH_3 flow rate (cm^3/min)	100
	Pressure (Pa)	200
	Deposition temperature (°C)	300
	LF ratio (%) / t_1 (s)/t_2 (s)	18% / 15/3

This paper presents a fabrication method of stress controllable SiN_x layer by PECVD. Low stress SiN_x layers were deposited in both HF mode and HF/LF mode. The achieved residual stress is in the range of 0—16 MPa, and has good repeatability. This paper can be a guide for other PECVD operators to better tailor a required film residual stress as a function of process parameters.

References

[1] B. Hoex, A. J. M. van Erven, R. C. M. Bosch, W. T. M. Stals, M. D. Bijker, P. J. van den Oever, W. M. M. Kessels and M. C. M. van de Sanden, Progress in Photovoltaics: Research and Applications **13**, 705 (2005).

[2] Wang S., Lennon A., Tjahjono B., Mai L., Vogl B. and Wenham S., Solar Energy Materials and Solar Cells **99**, 226 (2012).

[3] GAO Hong-sheng, WANG Zhen-zhen, XIE Yi-yang, GENG Zhao-xin, KAN Qiang, WANG Chun-xia, YUAN Jun and CHEN Hong-da, Journal of Optoelectronics · Laser **25**, 1338 (2014). (in Chinese)

[4] Wan Y., McIntosh K. R. and Thomson A.F., AIP Advances **3**, 032113 (2013).

[5] Wei J., Ong P. L., Tay F. E. H. and Iliescu C., Thin Solid Films **516**, 5181 (2008).

[6] Semenova O., Kozelskaya A., Zhi-Yong Li and Yu-De Yu, Chinese Physics B **24**, 06801 (2015).

[7] J. Yang, R. C. de Guzman, S. O. Salley, K. Y. S. Ng, B.-H. Chen and M. M.-C. Cheng, Journal of Power Sources **269**, 520 (2014).

[8] XIONG Xu-xu, JIANG Li-hua, ZENG Xiang-bin and ZHANG Xiao, Optoelectronics Letters **9**, 375 (2013).

[9] Lee S.-E. and Park Y.-C., Journal of Luminescence **161**, 154 (2015).

[10] Dergez D., Schalko J., Bittner A. and Schmid U., Applied Surface Science **284**, 348 (2013).

[11] Jiang H., Cao G., Xu C. and Zhang Z., Effects of Residual Stress in the Membrane on the Performance of Surface Micromachining Silicon Nitride Pressure Sensor, 15th International Conference on Electronic Packaging Technology, 664 (2014).

[12] Qin C. and Yin H., ECS Transactions **44**, 411 (2012).

[13] Karouta F., Vora K., Tian J. and Jagadish C., Journal of Physics D: Applied Physics **45**, 445301 (2012).

[14] Iliescu C., Wei J. S., Ong P. L. and Chen B. T., Low Stress PECVD SiN_x Process for Biomedical Application, CAS 2007 International Semiconductor Conference **1**, 139 (2007).

[15] LI Tian-wei, ZHANG Jian-jun, CAO Yu, HUANG Zhen-hua, MA Jun, NI Jian and ZHAO Ying, Optoelectronics Letters **10**, 202 (2014).

[16] Sah R. E., Baumann H., Driad R. and Wagner J., Journal of The Electrochemical Society **157**, G33 (2010).

[17] Tarraf A., Daleiden J., Irmer S., Prasai D. and Hillmer H., Journal of Micromechanics and Microengineering **14**, 317 (2004).

[18] Wang Y., Lee J., Thakur B. and Huang J., Dual Frequency Silicon Nitride Film of Low Thermal Budget for Pre-Metal Dielectric Applications in Sub-0.25 μm Devices, IEEE/SEMI Advanced Semiconductor Manufacturing Conference and Workshop, 405 (1999).