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EFFECT OF RAPID THERMAL ANNEALING ON THE PROPERTIES OF *μPCVD* AND *PECVD* SILICON NITRIDE THIN FILMS

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Thin silicon nitride films have been deposited on p-Si (100) substrates using optimised standard technological conditions in micro pressure chemical vapour deposition (μPCVD) and plasma enhanced chemical vapour deposition (PECVD) reactors at 760 ^{o}C and 380 ^{o}C respectively. The as-deposited films were annealed by rapid thermal annealing (RTA) at 800, 1000, 1200 and 1400 ^{o}C for varying annealing times: 15 -180 sec. The FTIR spectra showed that the Si-N characteristic peak moves to higher frequencies with annealing temperature increase. The etch rates in concentrated HF acid depends strongly on RTA temperature. The effect of RTA conditions on the dielectric strength, fixed charge density and hysteresis width has been determined.

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1. Introduction

Silicon nitride is most commonly deposited by different chemical vapor deposition (CVD) techniques. The CVD deposited thin films are dense, chemically inert, and are typically used for passivation in integrated circuit technology [1] and in the local oxidation of silicon [2]. The different CVD techniques are carried out at varying temperatures, which affects the properties of the films. Thermal decomposition and reaction of silicon containing reagents (SiH_2Cl_2 or SiH_4) and NH_3 at 800 ^{o}C is a characteristic of Micro-pressure CVD (μPCVD) [3]. Plasma Enhanced CVD (PECVD) is carried out below 400 ^{o}C, and uses an electrical discharge to decompose the chemical precursors [4]. It has been shown that these films have high hydrogen contents [5,6] in the form of Si-H and N-H bonds. The hydrogen incorporated in the silicon nitride films reduces the stress, but degrades the film stability. Because of the lower deposition temperature of PECVD thin films, the densities of these films are lower, and their etch rates are higher. Recently, some investigations of the post deposition annealing of the films have been carried out in order to establish their effect on the properties of the films [7-9]. The aim of this work is to carry out a comparative investigation of the influence of Rapid Thermal Annealing (RTA) at various temperatures: 800, 1000, 1200 and 1400 ^{o}C on the IR spectra, etching rates and electrical characteristics of silicon nitride films, fabricated by these two CVD techniques.

2. Experimental details

The silicon nitride films were deposited on p-type wafers, (100) oriented, with a resistivity of 4-6 ohm.cm. The deposition of the layers was carried out using two different reactor types - μPCVD and PECVD. The deposition parameters for the μPCVD reactor are: $T_{dep\,=}$ 767 ^{o}C and a ratio

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of reagents- SiH_2Cl_2/ NH_3 of 0.25.The correspondent parameters for the PECVD reactor are: 380 °C, SiH_4/NH_3 = 0.42. The thickness of the films was 100-120 nm. After the deposition, the samples were submitted to RTA in vacuum (5×10^{-5} torr) for varying times - 15, 30, 60 and 180 sec, at temperatures of 800, 1000, 1200 and 1400 °C. The RTA system raised the temperature from room temperature to the required value for 2 sec, and cooling down to 600 °C took for 7 seconds to perform. The samples were characterised by Refraction High Energy Electron Diffraction (RHEED), Fourier transform Infrared (FTIR) spectroscopy, and by the etching rates in 48% HF acid. The FTIR spectra were measured with a Bruker Analytische Messtechnik GmbH infrared analyzer. As μPCVD silicon nitride layers were deposited on both sides of the wafers, the silicon nitride layer was carefully removed from the unpolished reverse side of the wafer, using concentrated HF. Al dots were evaporated on the μPCVD and PECVD silicon nitride films through a mask, and a continuous aluminium film was deposited on the rear side of the wafers, forming MIS structures for assessing the electrical properties. After metallization, low temperature sintering was carried out to improve the contacts. The C-V curves were measured at high frequency (1 MHz), using a Boonton 72B capacitance meter with a test signal of 100 mV.

3. Results and discussion

RHEED investigations showed that both types of film (μPCVD and PECVD) are amorphous after deposition and remain amorphous after all RTA treatments.

The IR spectra of the as-deposited silicon nitride layers showed two major peaks: at 489.9 (μPCVD) and 429.5 cm^{-1} (PECVD) - attributed to the Si-N-Si symmetric bond-stretching vibration and 830.6 cm^{-1} (μPCVD) and 826.4 cm^{-1} (PECVD) - attributed to the asymmetric Si-N-Si bond-stretching vibration [10]. Fig. 1 shows a FTIR spectrum of a PECVD film annealed at 1400 °C for 3 sec. The effect of RTA at varying temperatures on the major peak position is given in Table 1.

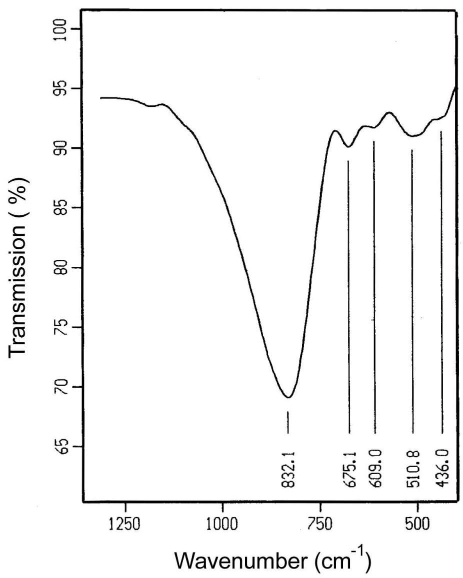

Fig. 1. FTIR spectrum of PECVD silicon nitride film after RTA at1400 °C for 3'.

As seen from Table 1, RTA has no significant effect on the position of the μPCVD and PECVD silicon nitride peaks, but on the whole they are shifted to higher frequencies for all temperatures. However, after RTA, large shifts of the peak corresponding to the symmetric Si-N-Si bond-stretching vibration of PECVD silicon nitride films have been reported by Beshkov *et al.* [11] The largest change corresponds to RTA at 1400 °C for 3 minutes - the peak shifts to 511 cm^{-1}.

The etch rates in 48% HF for the longest RTA duration (3 min) are also presented in Table 1. RTA reduces the etch rate of both types of silicon nitride specimen. As would be expected, the greatest decrease corresponds to the highest temperature. It is 21% for μPCVD and 37.5% for PECVD silicon nitride. The great difference in the etch rates of the two nitrides is due to their structural differences - μPCVD silicon nitride is highly stoichiometric, while PECVD films are non-stoichiometric and have a high hydrogen content. The larger reduction for PECVD layers is due to the greater changes which these layers undergo at high temperatures - the breaking of Si-H and N-H bonds and hydrogen out diffusion.

Table 1. Effect of RTA conditions on the major IR peak position and etch rates in 48% HF.

RTA conditions	Si-N-Si peak position [cm^{-1}]		Etch rate [nm/min]	
	μPCVD silicon nitride	PECVD silicon nitride	μPCVD silicon nitride	PECVD silicon nitride
As-deposited	830.6	826.4	9.5	40
3 min at 800 °C	833.3	823.9	9.5	36
3 min at 1000 °C	833.3	829.8	8.3	33.7
3 min at 1200 °C	832	829.9	7.7	30.3
3 min at 1400 °C	834.9	832.1	7.5	25

The breakdown voltage has been measured using a current of 1 μA as a criterion. The breakdown voltages per cm, i.e. the dielectric strengths for the as deposited layers and those with varying RTA temperatures are shown in Table 2.

Table 2. Dielectric strength of μPCVD and PECVD silicon nitride films [V/cm].

RTA conditions	μPCVD silicon nitride	PECVD silicon nitride
As-deposited	9.06×10^6	4.40×10^6
1 min at 800 °C	8.7×10^6	2.67×10^6
1 min at 1000 °C	8.7×10^6	4.15×10^6
1 min at 1200 °C	9.1×10^6	3.12×10^6
1 min at 1400 °C	9.06×10^6	1.38×10^6

The dielectric strength of μPCVD silicon nitride films is very high, indicating dense uniform films without structural defects. The high temperature and the low pressure of the reaction assure the formation of stoichiometric silicon nitride films without incorporated impurities of different character. The vertical position of the wafers is very important for the latter.

In contrast, low temperature PECVD silicon nitride films are non-stoichiometric and have high defect densities. There are lots of chargeable traps, inducing internal fields that bolster electric breakdown. The breakdown field of the PECVD silicon nitride layers is more than 2 times lower than that of μPCVD silicon nitride films. Although, as we have shown above, RTA reduces the etch rate of PECVD silicon nitride films, it degrades the electrical properties, leading to lower breakdown fields. In fact, half of the measured dots for the sample which was RTA annealed at 1400 °C were directly leaking. This was probably due to micro-crevices formed as a result of high stresses originating at such high temperatures.

We have made C-V measurements on the samples, to study the interface properties. A very wide hysteresis loop was observed for the PECVD films, while hysteresis was insignificant for μPCVD silicon nitride. The hysteresis is due to the charging and discharging of traps within the silicon nitride film. The counter-clockwise hysteresis corresponds to the injection of holes from the silicon surface, which is in accumulation. The hysteresis width for both nitride types after the varying RTA treatments is presented in Table 3. The high temperature stoichiometric μPCVD silicon nitride has very low chargeable interface state densities, which do not depend on RTA and remain nearly constant with temperature. However the densities of these chargeable traps increase rapidly with increasing RTA temperature for the PECVD silicon nitride films. These have a large number of defects, and it is well known that they contain silicon dangling bonds which are passivated by hydrogen, forming Si-H bonds. The RTA treatment most probably destroys these bonds, leading to a high density of chargeable traps and hence to a large hysteresis. However we have no data on PECVD silicon nitride films which underwent RTA at 1200 ^oC and 1400 ^oC. All the samples annealed for more than 15 sec. at these temperatures showed degradation of the accumulation capacitances: they were about 2-3 times lower than those for lower temperatures. Although we found many directly leaking dots at 1400 ^oC, that cannot explain the decreased accumulation capacitance. We suppose that these high temperatures bring about hydrogen out-diffusion, which leads to bubbles and results in a low density film [12]. The RTA has a small impact on the positive fixed charge of PECVD films (up to 1000 ^oC), but influences the fixed charge of μPCVD films: it increases at 1000 ^oC and decreases for higher temperatures.

Table 3. Effect of RTA treatments on fixed charge density and hysteresis width.

RTA conditions	μPCVD silicon nitride		PECVD silicon nitride	
	Fixed charge density [cm^{-2}]	Hysteresis width [V]	Fixed charge density [cm^{-2}]	Hysteresis width [V]
As-deposited	1.71E+12	0.29	1.30E+12	4.55
3 min at 800 ^oC	1.70E+12	0.36	1.22E+12	6.20
3 min at 1000 ^oC	2.59E+12	0.41	1.40E+12	9.08
3 min at 1200 ^oC	1.04E+12	0.15	—	—
3 min at 1400 ^oC	1.57E+12	0.32	—	—

4. Conclusions

Silicon nitride films deposited in two reactor types - μPCVD and PECVD - have been studied. The influence of RTA treatments on the positions of the IR peaks, the etch-rates, the dielectric strength, the fixed charge density and the hysteresis width have been examined. Although the RTA makes the films denser, it has a degrading effect on some interface properties; the latter being more pronounced in PECVD silicon nitride films.

References

[1] M. Sakamoto, M. Saito, K. Hamano, Jap. J. Appl. Phys. **21**, 147 (1982).
[2] T. Nozaki, T. Ito, H. Ishikawa, Proc. 17th Semiconductor IC Symposium, 108, 135 (1979).
[3] K. Niihara, T. Hirai, J. Mat. Sci. **11**, 593 (1976).
[4] R. Swan, R. Mehta, J. Cauge, J. Electrochem. Soc. **114**, 713 (1967).
[5] R. Chow, W. Lanford, W. Ke-Ming, R. Rosler, J. Appl. Phys. **53**, 5630 (1982).
[6] W. Lanford, M. Rand, J. Appl. Phys. **49**, 2473 (1978).
[7] M. Yoshimoto, T. Takubo, T. Saito, T. Ohtsuki, M. Komoda, H. Matsunami, IEEE Trans. El. Dev., **E75C**, 1019 (1992).
[8] L. Alexandrov, F. Edelman, Electron. Ind. **30**, 28 (1979).
[9] E. Irene, N. Chou, D. Dong, E. Tierney, J. Electrochem. Soc. **33**, 2518 (1980).
[10] G. Lucovsky, J. Yang, S. S. Chao, J. E. Tyler, W. Czubatyj, Phys. Rev. B **28**, 3234 (1983).
[11] G. Beshkov, D. Dimitrov, N. Velchev, P. Petrov, B. Ivanov, L. Zambov, T. Dimitrova, Vacuum, **58**, 509 (2000).
[12] G. Beshkov, D. Dimitrov, V. Lazarova, J. Koprinarova, K. Gesheva, E. Vlaev, J. Mater. Res. **12**, 2511 (1997).