

SILICON NITRIDE FILMS DEPOSITED BY ATMOSPHERIC PRESSURE CHEMICAL VAPOR DEPOSITION

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ABSTRACT

Films of silicon nitride are widely used in semiconductor technologies for very large scale integration (VLSI), thin film transistor (TFT), and solar cell applications. Current production technologies for silicon nitride use low pressure chemical vapor deposition (LPCVD) at temperatures > 700 °C or plasma enhanced chemical vapor deposition (PECVD) at temperatures below 450 °C. In this report, successful deposition of silicon nitride films by the low temperature thermal atmospheric pressure chemical vapor deposition (APCVD) method is described. Using a novel precursor tetraiodosilane (SiI_4), deposition of silicon nitride has been achieved at temperature as low as 400 °C. Data pertaining to the dependence of film properties on deposition temperature are presented, along with a evaluation of the deposition rate, composition, chemical structure, and conformality of the resulting films.

INTRODUCTION

Increasing semiconductor device integration by feature size reduction results in a higher number of interconnect levels and enhanced dependence on the properties and performance of dielectric materials [1]. Silicon nitride is of significant technical interest due to its extensive use in microelectronic device fabrication as passivation layer, as oxidation or diffusion barrier, and as interlevel isolation layer[2]. LPCVD is extensively used to deposit silicon nitride thin films at high temperatures range [3]. Excellent uniformity and high throughput can be achieved by using reaction of dichlorosilane and ammonia at a temperature of 700-800 °C. But the requirement of high deposition temperature of the LPCVD process has serious limitations for some advanced VLSI applications when low processing temperatures are required. For TFT applications, all the processing temperatures should be lower than 400 °C if low cost glass substrates are used [4]. PECVD is an established alternative for deposition of silicon nitride at low substrate temperatures ($<450^\circ\text{C}$) [5]. Silicon nitride films prepared by PECVD tend to be nonstoichiometric, and contain substantial quantities of atomic H (10-30%). However, the plasma process can cause ion bombardment damage of the underlying device structures. The high H concentration in the PECVD film is found to be related to the film instability and device degradation [6]. Deposition of low stress, low hydrogen content silicon nitride films with low surface damage at low temperature has been achieved by using microwave electron cyclotron resonance (ECR) deposition approach [7].

Atmospheric pressure thermal CVD using (TEOS/O_3) chemistry is a proven technology for depositing high quality silicon dioxide films at low temperatures . Thus,

it was the initial motivation of the research to apply the same technique for deposition of silicon nitride films at low temperatures by testing various precursor chemistries and deposition conditions. The obvious advantage of the APCVD technique over the conventional PECVD process is cost effectiveness due to the simpler tool design. This paper will focus on the development of APCVD process for low temperature deposition of silicon nitride films using SiI_4 as silicon precursor. The reaction of iodasilane and ammonia has been studied and supports the concept of a relatively stable intermediate monosilylamine. Although not explicitly directed toward CVD, the study indicates that at higher pressures trisilylamine and not silicon nitride is formed [8]. Recent recalculations of the bond dissociation energies of iodine and hydrogen bound to silicon [9], indicate that a preferred path to silicon nitride should avoid intermediates in which hydrogen is bound to silicon. Correlation between film properties and process parameters are presented, along with an evaluation of the deposition rate, composition, chemical structure, and conformality of the resulting films.

EXPERIMENT

Depositions were performed in a custom-designed rectangular CVD reactor system which incorporated a specialized Watkins Johnson monoblock injector (Fig1.). The wafer was seated on a quartz plate holder heated by resistance heating. The Substrate temperature was monitored by the thermocouple near the back surface of the quartz holder. Depositions were carried out on silicon at substrate temperatures of 300-550°C. All the deposition runs were performed at the fixed chamber pressure of 750 Torr.

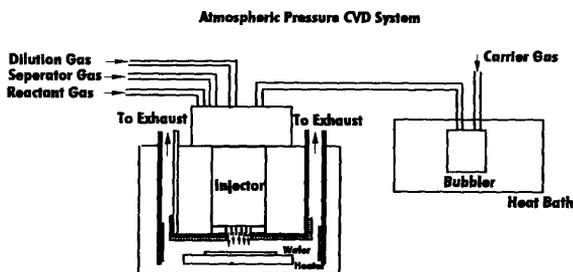


Fig1. Schematic of experimental set up.

SiI_4 was used as silicon precursor, and NH_3 as nitrogen precursor. High purity N_2 gas was used as carrier gas, and was also served as dilution and separator gas. Carrier gas and precursor flow to the inner zone of the injector; ammonia and dilution gas flow to the outside of the injector, while the separator gas flows in between. Such an injector design can effectively prevent the gas phase reaction. All the gas flow rates were regulated by mass flow controllers. Typical temperature for the SiI_4 bubbler was 170°C, carrier gas flow was used to control the precursor deliver rate. The precursor deliver line was heated to a temperature up to 20°C higher than the bubbler temperature to avoid recondensation.

Composition analysis was performed using Rutherford backscattering spectroscopy (RBS). Thickness and composition were determined by comparing measured spectra with simulations using the analysis program RUMP. Fourier transform infrared spectroscopy (FTIR) was used to determine the chemical bonding and H concentration in the films. Structure analysis was performed using x-ray diffraction(XRD). Conformality of the deposition was analyzed by scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Under the optimized processing window, series of runs were done in the temperature range from 350–550°C. RBS was performed for thickness and compositional analysis. The results are summarized in Table I. RBS spectrum of silicon nitride deposited at 400°C is shown at Fig2. The deposition of the silicon nitride film has been achieved at temperature as low as 350°C. The films are nitrogen rich at deposition temperatures below 550°C. There appears to be a trend toward stoichiometric deposition when the substrate temperature increases above 550°C. Unfortunately, due to the limitation of the sealing o-rings, the temperature could not be increased further. The iodine impurity concentration decreases dramatically when the substrate temperature increases from 350 to 400°C, and then decreases slowly with the further increase of the temperature. It was not clear why the growth rates increase greatly with the decrease of the deposition temperatures in the range between 350–450°C. The film obtained at 400°C has much lower impurity concentration than the film prepared at 350°C, and has film properties similar to the other high temperature runs. Accordingly, 400°C is considered to be a conservative minimum deposition temperature in this particular process window.

Table I. Temperature series runs

Bubbler temperature =170°C Injector temperature=200°C Flow rate: N2 carrier=0.1slm, NH3=1.0slm, N2 outzone=3.0slm, N2 innerzone=1.9slm N2 separator=1.9slm

Run#	Temperature (°C)	Growth Rate(A/min)	N/Si ratio	Iodine content (at.%)
243	350	1375	1.8	4.2
242	400	950	1.9	2.3
230	450	750	1.9	1.2
241	500	800	1.9	0.9
244	550	850	1.33	0.8

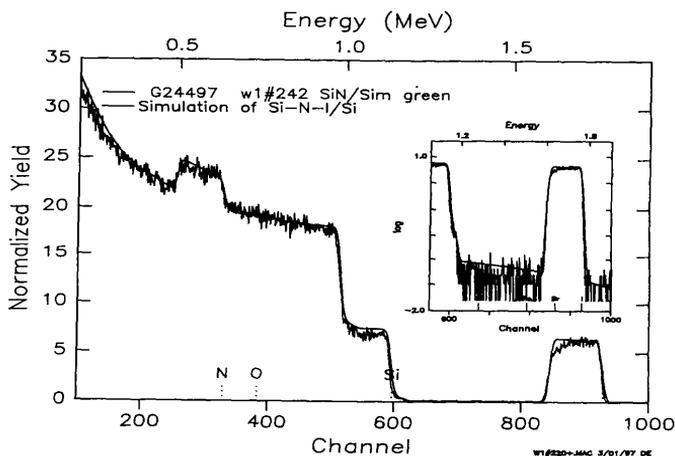


Fig.2 RBS spectrum of silicon nitride deposited on silicon at 400°C.

The infrared spectra for three silicon nitride films deposited at temperatures of 1) 350°C, 2), 400°C, and 3) 550°C are shown at Fig.3. All the deposited films showed strong N-H stretching mode at 3360 cm^{-1} and bending mode at 1200 cm^{-1} . Si-N stretching mode is at 880 cm^{-1} . The weak features near 2300 cm^{-1} were resulted from an incomplete subtraction of the absorption due to CO_2 in the spectrophotometer sample chamber. It is interesting that for our specific process, no Si-H bonding configuration (at 2180 cm^{-1}) has been observed in the FTIR spectra. The Asymmetry of the N-H stretching mode peaks is due to the hydrogen bonding between the H atoms in the N-H bonds and long-pair electrons on nearby N atoms[10]. The temperature dependence of the N-H concentration is shown in Fig.4. The N-H concentration is calculated based on the calibration results from W.A.Lanford [11] and H.Efstathiadis [12]. The typical N-H concentration for films deposited at temperature $>400^\circ\text{C}$ is around $4.0 \times 10^{22}/\text{cm}^3$. Since there is no Si-H bonding in the film, the N-H bonding concentration could be used to indicate the H concentration in the film assuming a weak concentration of unbonded hydrogen. The films have absolute H concentrations around 30%, which are similar to the typical PECVD deposited silicon nitride films. The positions of the Si-N and N-H stretching modes are found to be sensitive to the hydrogen content in the films. The Si-N stretching mode will shift to the high wavenumber direction, and N-H stretching mode shift to the low wavenumber direction as the H content in the film increases.

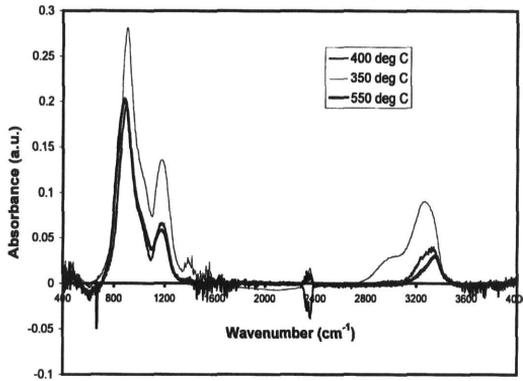


Fig.3 Infrared absorbance spectra for three silicon nitride films deposited at different substrate temperature

XRD diffraction measurements showed that the deposited films were amorphous. Scanning electron microscopy showed a conformal deposition of silicon nitride over a 1×1.6 micrometer feature size trench structure with 10 nm TiN (Fig.5) on top, the step coverage is better than 85%. Comparing SEM thickness measurement with the results from the RBS, the film density of the moderate temperature (450°C) runs is calculated to be 2.4 g/cm^3 , which is comparable to typical PECVD results.

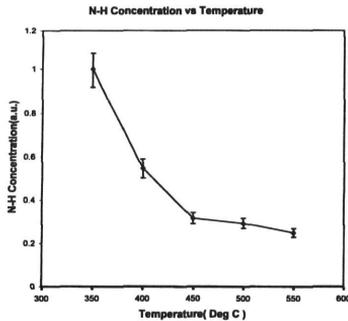


Fig.4 FTIR N-H concentration versus substrate temperature.

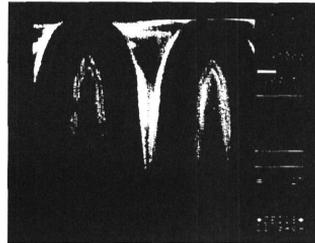


Fig.5 Cross section-SEM of 380 nm SiN grown on top of TiN trench structure with feature size $1 \times 1.6 \mu\text{m}$.

CONCLUSIONS

It has been demonstrated that silicon nitride films can be grown by thermal APCVD at temperature as low as 400°C using SiL₄ and NH₃ chemistry. The film properties such as stoichiometry, impurity and H concentration, and growth rate are strongly dependent on the deposition temperature. No Si-H bonding configuration exists in the deposited films. Under moderate deposition temperature film density is about 2.4g/cm³. and H concentration is around 30%. These properties are comparable to the film prepared by PECVD process. Further investigation will be conducted to optimize the processing parameters to lower the impurity and H concentration, and increase the density of the film.

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