

Deposition and characterization of silicon carbon nitride films prepared by RF-PECVD with capacitive coupling

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Abstract: The goals of this work were to synthesize stoichiometric silicon carbon nitride ($\text{Si}_{1.5}\text{C}_{1.5}\text{N}_4$) films using the RF-PECVD method and to characterize the deposited material. Gas mixtures, as opposed to an organic monomer, were chosen for reactants. Gas mixtures allow for varying the concentration of the elements needed for silicon carbon nitride synthesis and thereby optimizing the composition of the deposited films. It was found that amorphous hydrogenated silicon carbon nitride films having low oxygen contamination and comparable concentrations of silicon and carbon but deficient in nitrogen could be prepared by RF-PECVD from gas mixtures of silane, methane and nitrogen. The methane concentrations in the reactant gas mixture and flow rate or residence time were found to be important variables in achieving this objective. The chemical composition, structure and morphology of the films were studied by XPS, HFS, FTIR, XRD and AFM. These data suggested that silicon bonding in the films was analogous to that in silicon carbide and silicon nitride while carbon was bonded as carbide carbon and nitrogen as nitride nitrogen. The deposited films adhered well to silicon wafers, aluminum and mild steel with minimum pretreatment prior to deposition. The refractive index and density of representative silicon carbon nitride films are also reported.

Keywords: silicon carbon nitride; thin films; plasma deposition; composition; structure

1. Introduction

In a 1985 publication [1], Cohen first suggested that a covalent solid formed between carbon and nitrogen could have a larger bulk modulus than diamond. In a subsequent publication [2], Liu and Cohen stated that "On the microscopic level, for ideal systems, hardness is determined by the bulk modulus, which in turn depends on the nature of the chemical bonding." In this same publication the authors presented a theoretical scaling law relating the bulk modulus to bond length and ionicity for zinc-blend solids. Using this scaling law, a carbon-nitrogen bond length of 1.47 Å and an ionicity of 1/2 [2], one can calculate a bulk modulus for crystalline beta carbon nitride ($\beta\text{-C}_3\text{N}_4$) of 4.83 Mbar. For comparison, the bulk modulus of diamond, the hardest known solid, is 4.43 Mbar. Following the work of Cohen, many laboratories, using a variety of deposition methods [see, for example, refs. 3 through 15] have attempted to reproducibly synthesize super hard, high purity, crystalline $\beta\text{-C}_3\text{N}_4$ thin films. To date, these efforts have met with only limited success [16, 17].

Early on in this research, efforts were also made to synthesize carbon nitride films using the inductively coupled plasma – chemical transport reaction (ICP-CTR) method [9]. The reactants were high purity nitrogen gas for the plasma and two different solid carbon reactants, a high surface area activated carbon fabric (surface area = 1600 m^2/g) and low surface area carbon (graphite) foam. During the course of the research several difficult prob-

lems were encountered. It was found that the carbon nitride films were contaminated with 23.5-35.5 atomic% hydrogen in the bulk from an unidentified source. Hydrogen is thought to interrupt the growing network formed by C and N due to the attachment of H to C and/or N [18] and thereby inhibit the formation of hard $\beta\text{-C}_3\text{N}_4$. Also, the films were deficient in nitrogen relative to stoichiometric carbon nitride. The bulk nitrogen concentration in the deposited films was in the range 33.5 to 37.8 atomic%, i.e., consistently lower than the 57.1 atomic% found in $\beta\text{-C}_3\text{N}_4$. The average deposition rates were very low, 0.92-2.3 nm/min, which was attributed to a decrease in rate of deposition with time caused by reaction of the nitrogen plasma with the surface of the solid carbon sources.

As a result of the difficulties encountered in attempting to synthesize high quality carbon nitride films the research was redirected to the synthesis of silicon carbon nitride [17]. This paper describes the results of the redirected effort. The goals of this work were to synthesize stoichiometric silicon carbon nitride ($\text{Si}_{1.5}\text{C}_{1.5}\text{N}_4$) films using the RF-PECVD method and to characterize the deposited material. Gas mixtures, as opposed to an organic monomer, were chosen for reactants. Gas mixtures allow for varying the concentration of the elements needed for silicon carbon nitride synthesis and thereby optimizing the composition of the deposited films. The film composition, structure and morphology were determined using XPS, FTIR, XRD and AFM. The refractive index, de-

position rate and density of typical silicon carbon nitride films are also reported.

2. Experimental details

Reactant gases and supplier's stated purity: silane (SiH_4) 99.99%, methane (CH_4) 99.99%, nitrogen (N_2) 99.999+%. All gases were used without further purification except for the base gas mixture of 1% SiH_4 , 1% CH_4 and the balance N_2 . This base gas mixture flowed through a Supelco OMI-2 Indicator Tube to remove traces of oxygen before entering the reaction chamber.

Substrates: The majority of the films were deposited on 1 inch (2.54 cm) diameter single side polished silicon wafers {P-type boron doped, (100) orientation, 1-20 ohm-cm resistivity} of 250-300 microns thickness. A few coatings were deposited on 1018 mild steel and aluminum disks. The silicon wafer substrates were used as received from the supplier without cleaning before being placed in the deposition chamber. The mild steel and aluminum substrates were cleaned for several minutes at an elevated temperature in an ultrasonic cleaner containing an aqueous detergent solution. They were then rinsed with acetone and dried before being coated. The effectiveness of this cleaning procedure was determined by using the cellophane tape test for adhesion. This test revealed that the silicon carbon nitride coatings adhered very well (no film fragments were removed by the tape) to the metals and silicon substrates.

Deposition system: A modified SAMCO International, Inc., Model PD10 plasma enhanced chemical vapor deposition system was used to prepare the silicon carbon nitride thin films. Vacuum integrity of the deposition system was checked with a Dycor Model X RGA (residual gas analyzer) and helium spray. No detectable air leaks were found. Fig. 1 shows a cross-section of the RF-PECVD deposition chamber. The Pyrex glass chamber was 30.5 cm long and 7.63 cm diameter with a glass-to-metal seal at each end for attachment to a metal vacuum flange. A removable aluminum liner covered

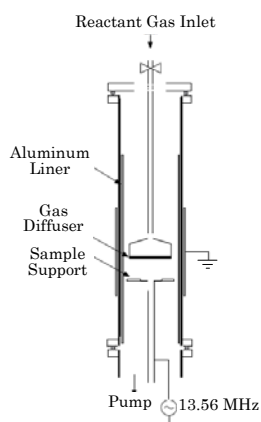


Fig. 1 Plasma deposition chamber

the inside surface of the chamber to assist in cleaning deposited material from the wall. A grounded aluminum electrode was attached to the outer surface of the chamber. A gas diffuser, located 2.54 cm from the surface of the substrates, was used to uniformly distribute the reactant gas mixtures over the substrate surfaces. The diffuser was made from a My-

krolis Wafergard III NF-75 inline gas filter. The sample support was made from stainless steel and connected to an RF Services, Inc. (Model: Training Match) auto-matching unit and Advanced Energy Model RFX-600 13.56 MHz power supply.

Deposition procedure: At the start of a deposition experiment, a substrate was placed in the recess located on top of the sample support shown in Fig. 1, the deposition chamber was then sealed and evacuated to a background pressure of 0.13 Pa using a Roots-type pump backed by an oil-sealed mechanical pump. A flow of nitrogen was started and a plasma was struck for 5 minutes to condition the reaction chamber before flushing it for 5 minutes with the desired reactant gas mixture. The reactant gas composition was changed by flowing varying amounts of pure CH_4 into the base gas mixture of 1% SiH_4 , 1% CH_4 and the balance N_2 .

Analytical instrumentation:

XPS (X-ray Photoelectron Spectroscopy): A PHI Quantum 2000 Instrument, X-ray source: monochromated Al $K\alpha$ 1486.6 eV, acceptance angle $\pm 23^\circ$ and takeoff angle 65° was used for XPS analysis of the films. 4 keV Ar^+ (argon ion) were used for removing surface oxide from the silicon carbon nitride films and for depth profiling prior to XPS analysis. The thickness of the silicon carbon nitride layer removed by Ar^+ sputtering was estimated from the removal rate of silicon dioxide (~ 10.8 nm/minute).

HFS (Hydrogen Forward Scattering): A Charles Evans and Associates, Model RBS400 instrument was used to measure the bulk concentration of hydrogen in the silicon carbon nitride films. The instrument settings used for HFS analysis were: helium ion beam energy of 2.275 MeV and the HFS detector at 30 degrees from the forward trajectory of the helium ion beam.

FTIR (Fourier Transform Infrared): A Thermo Nicolet Magna 550 FTIR spectrometer with a Thermo Spectra Tech NicPlan FTIR Microscope in transmission mode was used for FTIR spectral analysis.

Ellipsometry: A custom built discrete wavelength ($\lambda = 632.8$ nm) ellipsometer (Model PHE-101) made by Microphotronics, Inc. was used for film thickness and refractive index measurements.

AFM (Atomic Force Microscopy): A Digital Instruments Dimension 3000 with an etched silicon probe in the trapping mode, a scan rate of 0.5 Hz and with a set point that was 67 % of the free-standing RMS voltage was used for roughness measurements.

XRD (X-ray Diffraction): A Phillips X' Pert MRD diffractometer with a copper anode source operated at 45 kVA-40mA was used to investigate the crystallinity of the films.

Film weight: A Cahn Model C-31 Microbalance was used to measure the weight of the silicon carbon nitride films deposited on glass cover slips of known area.

3. Results and discussion

Fig. 2 shows XPS depth profile plots for the major elements found in a representative silicon carbon nitride film deposited on a silicon wafer by RF-PECVD. This graph shows that the pre-sputter oxygen (O) concentration is ~28 atomic% whereas the concentration after the first Ar+ sputter cycle of 30 seconds (~5.4 nm silicon dioxide equivalent) the concentration dropped to ~2 atomic%. Subsequent sputter steps through the remainder of the film found O to stabilize at ~1 atomic%. These data suggested that the high levels of O detected at the sample surface are primarily or solely attributed to surface oxidation. It is also evident from the plots that the concentrations of silicon and carbon are comparable whereas the concentration of nitrogen is consistently lower throughout the bulk of the film. (A subsequent reference to “bulk” in this manuscript means the composition determined by XPS analysis after 5 minutes of Ar+ sputtering to remove the oxidized surface layer.)

Shown in Table 1 is the bulk oxygen concentration derived from XPS analysis of samples of silicon carbon nitride films deposited using different reactant gas mixture flow rates. These data show that the bulk oxygen concentration increased from an average 2.6 to 15.7 atomic% when the flow rate was decreased from about 185 to 153 ml/min. Shown in Table 2 is the bulk oxygen concentration of samples of silicon carbon nitride deposited at different methane concentrations in the reactant gas mixture. These data show that the oxygen concentration remained about the same when the methane concentration was increased from 1 to 21%. In summary, the concentration of oxygen in the bulk of the silicon carbon nitride films was found to be independent of the methane concentration in the feed gas at total flow rates in excess of 170 ml/min or a residence time in the reaction zone between the diffuser and the silicon wafer substrate of ~0.01 second at 33 Pa.

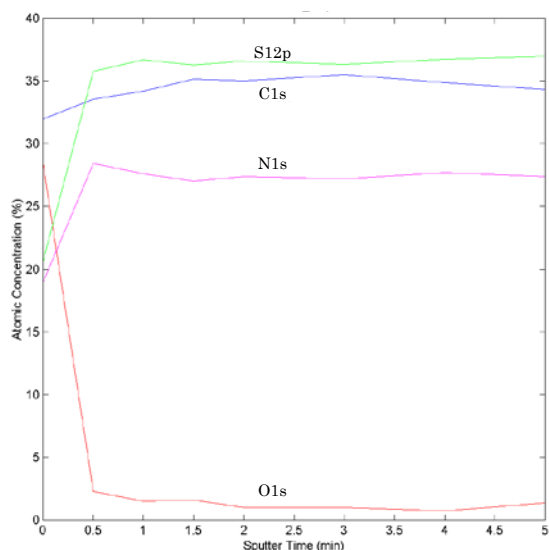


Fig. 2 XPS depth profile analysis of a silicon carbon nitride film

Table 1. Effect of the reactant gas mixture flow rate on the bulk oxygen concentration in some representative silicon carbon nitride films

Sample ID	Flow Rate, ml/min	Reactant Gas Composition, %	Bulk O conc., atomic%
SiCNG-213	188	18% CH ₄ , 0.8% SiH ₄ bal. N ₂	2.4
SiCNG-214	183	21% CH ₄ , 0.8% SiH ₄ bal. N ₂	2.8
SiCNG-195	164	20% CH ₄ , 0.8% SiH ₄ bal. N ₂	14.7
SiCNG-197	153	20% CH ₄ , 0.8% SiH ₄ bal. N ₂	16.7

Table 2. Effect of the methane concentration in the reactant gas mixture on the bulk oxygen concentration in some representative silicon carbon nitride films

Sample ID	Flow Rate, ml/min	Reactant Gas Composition, %	Bulk O conc., atomic%
SiCNG-157	170	1% CH ₄ , 1% SiH ₄ bal. N ₂	2.8
SiCNG-160	170	1% CH ₄ , 1% SiH ₄ bal. N ₂	2.9
SiCNG-161	170	1% CH ₄ , 1% SiH ₄ bal. N ₂	2.7
SiCNG-213	188	18% CH ₄ , 0.8% SiH ₄ bal. N ₂	2.4
SiCNG-214	183	21% CH ₄ , 0.8% SiH ₄ bal. N ₂	2.8

The source of oxygen found in the bulk of the silicon carbon nitride samples is thought to be background oxygen present in the deposition chamber [19]. At low flow rates, the rate of oxygen reaction with the growing silicon carbon nitride film is significant relative to the deposition rate and thereby leading to a higher oxygen concentration in the film. Conversely, at high flow rates, the deposition rate is significantly greater than the rate of reaction of oxygen with the growing film and the oxygen concentration in the film is lower.

The conclusions derived from the parametric studies of flow rate and methane concentration were used to optimize the deposition conditions for depositing near stoichiometric silicon carbon nitride $\{(Si_{1.5}C_{1.5}N_4), [17]\}$ films having a minimum bulk concentration of oxygen. The following preferred deposition conditions were then used for depositing additional silicon carbon nitride films having a low bulk oxygen concentration:

- Gas composition: 20% CH₄, 1% SiH₄, balance N₂
- Total flow rate: >170 ml/min; residence time <0.01 s at 27-33 Pa
- Pressure: 0.20-0.25 Torr (27-33 Pa)
- 13.56 MHz RF power: 100 Watts forward, 2-4 Watts reflected
- Deposition time: 20 minutes

Table 3 shows the bulk composition derived from XPS analysis of some representative silicon carbon nitride films deposited at two different reactant gas compositions. It is evident from this data that the carbon concentration in the films is much lower when the concentration of methane in the feed gas is lower. This finding shows that by varying the composition of the reactant gas mixture the composition of the deposited films can be changed and optimized. The data in Table 3 also shows that in films deposited with 20% methane in the feed gas the silicon and carbon concentrations are consistently higher while

Table 3. Bulk composition (atomic%) of several representative silicon carbon nitride films derived from XPS analysis

Sample ID	Si	C	N	O	Flow Rate, ml/min
Si _{1.5} C _{1.5} N ₄ [17]	21.4	21.4	57.1	0.0	
SiCNG-157 (a)	52.2	8.7	36.4	2.8	170
SiCNG-160 (a)	52.1	9.5	35.6	2.9	170
SiCNG-161 (a)	52.1	8.7	36.6	2.7	170
SiCNG-151 (b)	31.9	38.7	26.7	2.6	170
SiCNG-201 (b)	33.1	39.0	25.4	2.5	178
SiCNG-207 (b)	32.0	39.1	25.0	3.9	162
SiCNG-210 (b)	32.3	39.7	24.3	3.7	162
SiCNG-213 (b)	33.8	37.0	26.9	2.4	188
SiCNG-214 (b)	32.5	39.5	25.3	2.8	183

(a) Reactant gas composition: 1% CH₄, 1% SiH₄, bal. N₂
 (b) Reactant gas composition: 20% CH₄, 0.8% SiH₄, bal. N₂

the nitrogen concentration is significantly lower than the concentration in Si_{1.5}C_{1.5}N₄. The lower than desired bulk nitrogen concentration in the films may be related to the difficulty in activating nitrogen in the RF plasma due to the strong triple bond in elemental nitrogen (225.94 kcal/mol bond energy [20]).

It is of interest to identify any correlation between the chemical composition of the reactants and the composition of the silicon carbon nitride films deposited when using a gas mixture (this work) or organic monomer [19, 21]. To allow for this comparison, the Si/N and Si/C elemental ratios were chosen to reflect the chemical composition of the reactants and the films. From the film/reactants ratios shown in Table 4, it is clear that there is generally no correlation between the elemental composition of the films and the reactants. Only in the case of the Si/C ratio in the Izumi et. al work is the elemental ratio in the film comparable to the ratio in the reactant.

Table 5 shows a comparison between the stoichiometry of silicon carbon nitride films prepared in this work and those prepared by others [19] using the single-source precursor bis(trimethylsilyl)carbodiimide (C₇H₁₈N₂Si₂) and the RF-PECVD method. The films prepared by Zhou et. al, Table 5, were deposited on the RF electrode

Table 4. Elemental ratios in the silicon carbon nitride films versus the reactants

Authors	Elemental Ratios				Film/Reactants Ratio	
	Reactants		Film			
	Si/N	Si/C	Si/N	Si/C	Si/N	Si/C
This work	0.01	0.04	1.27	0.84	127	21
Zhou et. al [19]	1.00	0.28	0.57	0.91	0.57	3.25
Izumi et. al [21] (a)	2.00	0.33	0.68	0.32	0.34	0.97

(a). without ammonia additive

Table 5. Comparison between the stoichiometry of silicon carbon nitride films prepared in this work and those prepared by Zhou et. al [19]

Sample ID	Stoichiometry
SiCNG-213	Si _{0.79} C _{1.09} O _{0.07} H _{1.09}
SiCNG-214	Si _{0.78} C _{1.21} O _{0.09} H _{1.26}
Zhou et. al	Si _{1.89} C _{1.10} O _{0.04} H _{1.00}
Zhou et. al	Si _{1.64} C _{1.09} O _{0.10} H _{1.24}

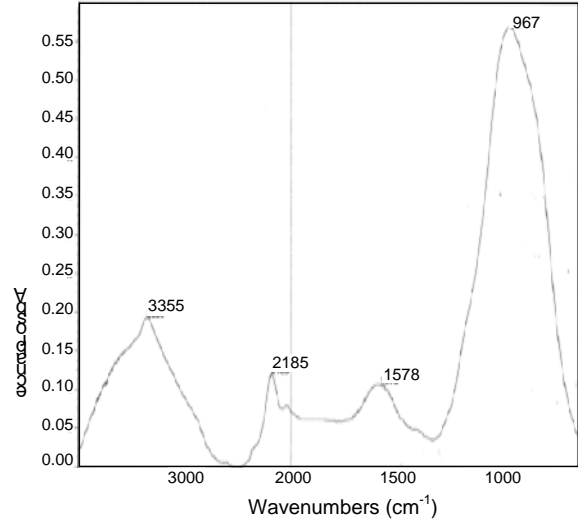


Fig. 3 FTIR spectrum of silicon carbon nitride film

(as in this work) and the bulk composition was determined using glow discharge optical emission spectroscopy. The stoichiometry of the samples prepared in these two studies is very similar except for the amount of nitrogen. The samples prepared from C₇H₁₈N₂Si₂ are much richer in nitrogen than those prepared from the gas mixture.

Fig. 3 is an FTIR spectrum of a silicon carbon nitride film on a silicon wafer. Table 6 shows the assignments made to the absorption bands shown in the spectrum. These assignments were made based on the assignments and references reported by Zhou et. al [19]. These authors also showed an FTIR spectrum of a silicon carbon nitride film deposited on S652 stainless steel and assigned the absorption bands in their spectrum to N-H, C-H, C=N, N=C=N, C=N and Si-C bonds. The major difference between the FTIR spectrum recorded in this work and that of Zhou et. al is the presence of the strong broad absorption band at 967 cm⁻¹ peak found here. This band may be assigned to both Si-N and Si-C combined. The Si-C (780 cm⁻¹) and Si-N (950 cm⁻¹) bands in bulk are generally reported to be broad [19].

High resolution XPS spectra for Si2p, C1s, and N1s core electrons are shown in Fig. 4. These spectra were obtained from the bulk of a silicon nitride film. The electron binding energy at the peak maximum for these

Table 6. FTIR absorption band assignments

Bond/functional group	Wave number, cm ⁻¹
Si-C (bulk)	780 (right shoulder on 967 cm ⁻¹ peak)
Si-N (bulk)	967
C-C	1400
C=C	1578
Si-H (stretching modes)	~2050
N=C=N	2185
C-H (aliphatic & aromatic)	~2900 (shoulder)
N-H	3355

Table 7. Comparison between the peak maximum S2p, C1s and N1s electron binding energies from the bulk of a silicon carbon nitride film with binding energies in silicon nitride, silicon carbide and ammonium

	Binding Energy, eV			
	Si2p	C1s	N1s	
SiCNG-213	100.3	283.0	396.8	402.6
Others	100.6 (Si ₃ N ₄) [22] 100.3 (SiC) [26]	282.9 (SiC) [23]	397.5 (Si ₃ N ₄) [24]	402 (NH ₄ Cl) [25]

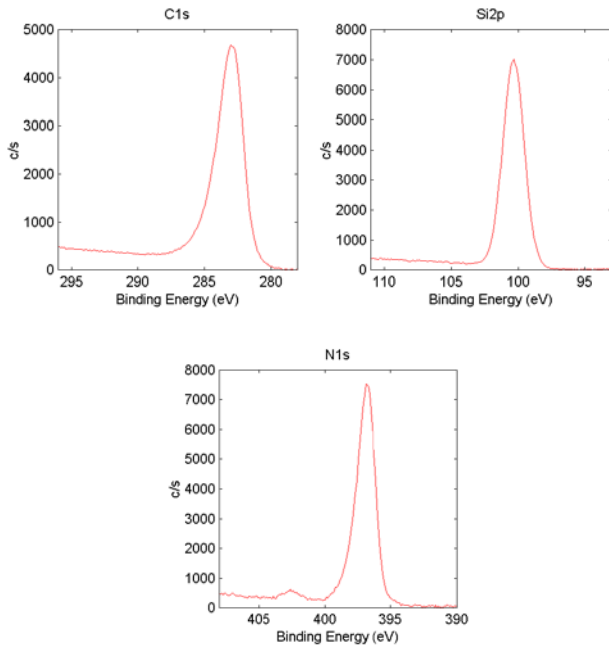


Fig. 4 High resolution XPS analysis of the Si2p, C1s, and N1s peaks derived from the bulk of a silicon carbon nitride film

three elements is shown in Table 7. For comparison, Table 7 also shows the binding energy reported by others for these elements when present in silicon nitride (Si₃N₄), silicon carbide (SiC) and ammonium chloride. The good agreement between the binding energies for carbon and nitrogen in the silicon carbon nitride film bulk and SiC and Si₃N₄ suggests that carbon bonding in the film is analogous to carbide carbon and nitrogen bonding is analogous to nitride nitrogen. Likewise, the good agreement between the core electron binding energies for silicon in the bulk silicon carbon nitride film and silicon in SiC and Si₃N₄ suggests that silicon is present in both carbide and nitride chemical bonding in the silicon carbon nitride film. This suggestion is further supported by the work of others who have deconvoluted the high resolution peak for Si2p from a silicon carbon nitride film into two peaks, one assigned to silicon carbide and one to silicon nitride [21]. The weak peak shown in Fig. 4 for N1s at 402.6 eV is very close to the binding energy of the N1s electron found in ammonium chloride.

XRD analysis was used to determine if the plasma deposited silicon carbon nitride films were amorphous or crystalline. The films prepared here were amorphous as

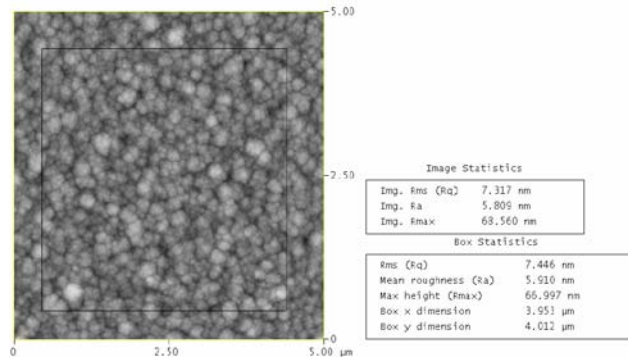


Fig.5 Photograph obtained by AFM analysis of the surface of a silicon carbon nitride film

Table 8. Refractive index at $\lambda = 632.8$ nm and deposition rate of silicon carbon nitride films deposited under preferred conditions

Sample ID	Refractive Index	Thickness, nm (a)	Deposition Rate, nm/min
SiCNG-196	2.6105	1245.71±14.13	62.28
SiCNG-201	2.6208	1263.42±18.63	63.17

a. Average thickness and standard deviation derived from five thickness measurements made at different locations on the silicon wafer using ellipsometry

evidenced by the lack of any crystalline or diffraction peaks in the XRD spectrum. Fig. 5 is a photograph of the surface of a silicon carbon nitride film derived from AFM analysis. The root mean square roughness (Rq) of this typical sample was 7.446 nm, average roughness (Ra) 5.91nm and maximum height (Rmax) 66.997.

Table 8 shows the refractive index and thickness of representative samples of plasma-deposited silicon carbon nitride films on silicon wafers. For comparison purposes, the refractive index of plasma-deposited silicon carbide ranges from 1.96 to 2.6 and plasma-deposited silicon nitride from 1.8 to 2.2 [27]. The film thickness and deposition time was used to calculate the deposition rates shown in Table 8. The weight of silicon carbon nitride films deposited on glass cover slips of known area and measured thickness using ellipsometry were used to calculate the density of three different films. The calculated density was 2.93, 2.99 and 2.96 g/cm³. For comparison purposes, the density of plasma-deposited silicon nitride ranges from 2.1 to 3.1 g/cm³ depending on the major deposition variables [27].

4. Conclusions

Amorphous hydrogenated silicon carbon nitride films were successfully synthesized from a gas mixture of silane, methane and nitrogen by the RF-PECVD method with capacitive coupling. The concentration of carbon in the films was varied by changing the concentration of methane in the reactant gas mixture. The surface of the films was highly oxidized but the thickness of the oxidized layer was only ~5.0 nm. The reactant gas flow rate or residence time was found to be an important variable for controlling the amount of oxygen contamination in

the bulk of the deposited films. The films had about the same concentration of silicon and carbon but were deficient in nitrogen when compared with stoichiometric silicon carbon nitride. Chemical bonding of the silicon in the films appeared similar to that in silicon nitride and silicon carbide based on XPS and FTIR analyses. The majority of the nitrogen appeared as nitride nitrogen and the carbon as carbide carbon.

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