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Citation for published version (APA):

Boher, P., Renaud, M., IJzendoorn, van, L. J., & Hily, Y. (1989). Hydrogen and oxygen content of silicon nitride films prepared by multipolar plasma-enhanced chemical vapor deposition. *Applied Physics Letters*, 54(6), 511-513. <https://doi.org/10.1063/1.100915>

DOI:

[10.1063/1.100915](https://doi.org/10.1063/1.100915)

Document status and date:

Published: 01/01/1989

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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- The final published version features the final layout of the paper including the volume, issue and page numbers.

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Hydrogen and oxygen content of silicon nitride films prepared by multipolar plasma-enhanced chemical vapor deposition

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(Received 6 September 1988; accepted for publication 25 November 1988)

Very low H content SiN films have been deposited by a multipolar plasma-enhanced deposition system at room temperature. The main plasma parameters which control the hydrogen and oxygen incorporation in the films have also been analyzed and optimized.

Silicon nitride films are now widely used as insulating interlayers and final passivation films for integrated circuit technology. On III-V compounds like GaAs or GaInAs, these films must be prepared at low temperature ($< 300^\circ\text{C}$) without ionic bombardment. Numerous methods have been developed to deal with this problem including chemical vapor deposition (CVD), and related methods like plasma-enhanced chemical vapor deposition (PECVD), or photo-CVD. Unfortunately these methods generally use hydrogenated gases like SiH_4 and NH_3 which result in SiN films with high hydrogen concentration. High H contents in the films induce some problems such as parasitic conduction due to hot-electron trapping in the insulator¹ or degradation after thermal treatments.² A method which uses a silicon target instead of silane with an ion beam sputtering system has also been developed to avoid H incorporation.³ Unfortunately the high degree of bombardment of the surface makes this method difficult to use for the encapsulation of III-V compounds.

A new method based on an ultrahigh vacuum system with a multipolar plasma enhanced by a hot filament has been developed in our group and described in another paper.⁴ Multipolar plasma chemical vapor deposition (MPCVD) Si_3N_4 films were deposited on some substrates (Si, GaAs, and GaInAs) and the plasma conditions were varied. The chemical and electrical properties of the films were measured. We showed that the deposition rate and the oxygen content of our films depend strongly upon the flux ratio of the gases used in the system [pure N_2 and diluted SiH_4 (10% in Ar)]. Moreover, we demonstrated that these parameters are directly correlated with the interface state density measured on $\text{TiAu/Si}_3\text{N}_4/\text{GaInAs}$ metal-insulator-semiconductor (MIS) structures. In this letter we analyze more precisely the hydrogen and oxygen contents of our films and their dependence on the plasma parameters. A comparison with classical PECVD Si_3N_4 films is also made.

The MPCVD deposition system has been presented previously.⁴ Here we want to point out that the electrons emitted by a hot filament are accelerated by an applied bias V_f between the source and the magnetic container. The magnetic confinement is ensured by permanent magnets mounted on the walls of the chamber. To adjust the characteristics of the plasma four parameters can be changed: (1) the filament

bias V_f , (2) the discharge current between filament and vessel I_f , (3) the total pressure of the gases admitted in the vessel, and (4) the composition of the gases admitted in the vessel which is represented in the SiN deposition case by the SiH_4/N_2 flux ratio. In the present study, we have only varied the flux ratio of the gases. We have demonstrated previously that this parameter has the most important impact on the composition of the SiN film.⁴

Deposition rates were evaluated by spectroscopic ellipsometry (SE) in the range 1.6–5.4 eV.⁵ The Si, O, and N content of the films was measured with Rutherford backscattering spectrometry (RBS) using 2 MeV He^+ ions. The hydrogen content was evaluated in the same target chamber using elastic recoil detection (ERD). For this purpose a detector was positioned at a scattering angle of 30° and a 9- μm -thick Mylar foil was used to selectively stop the forwardly scattered He ions.

The deposition conditions and atomic contents of eight of our MPCVD films, deposited on unheated ($T < 100^\circ\text{C}$) GaAs substrates, are listed in Table I. The SiH_4/N_2 flux ratio was varied between 1.4 and 2.5% while other plasma conditions were fixed ($V_f = -75\text{ V}$, $I_f = 100\text{ mA}$, total pressure at 7 mTorr). Before the deposition all the samples have been submitted to a hydrogen multipolar plasma in order to remove completely the native oxide at the surface.⁶ This precaution ensures that the oxygen content measured by RBS is the effective content of the SiN film. Two classical PECVD films obtained at two different substrate temperatures in an industrial system with optimized plasma conditions are also reported in Table I.

The first observation is that our films have a very low hydrogen content compared to PECVD films. The hydrogen content of our PECVD films is nevertheless in agreement with the results reported in the literature (from 15.4 to 30.7% for standard deposition systems in Ref. 7). Up to now the hydrogen content of our MPCVD SiN films ($< 8\%$ for the best one) has been reached only by low-pressure CVD methods^{7,8} which involve higher deposition temperature (around 800°C), and which are not suitable for III-V encapsulation.

Second, the dependence of the deposition rate on the flux ratio is quite surprising. This dependence is represented in Fig. 1. The deposition rate reaches a minimum around $\text{SiH}_4/\text{N}_2 = 1.7\%$. This behavior suggests a complex mechanism which involves more than one chemical reaction. The main chemical reaction

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TABLE I. SE, RBS, and ERD results on some MPCVD and PECVD SiN films. (a) The MPCVD films are deposited on GaAs substrates varying only the SiH_4/N_2 flux ratio ($V_f = 75$ eV, $I_f = 100$ mA, total pressure 7 mTorr). (b) The PECVD films are deposited on Si substrates varying the substrate temperature. The thicknesses and deposition rates are deduced from SE measurements. Si, N, O, and H contents are deduced from RBS and ERD measurements (in % of the total atomic content). The error on the different atomic contents is evaluated around 2%.

(a) MPCVD SiN films.							
Sample	SiH_4/N_2 (%)	Thickness (Å)	Dep. rate (Å/min)	Silicon (%)	Nitrogen (%)	Oxygen (%)	Hydrogen (%)
1	2.5	569	19.1	34	43	13	9
2	2.4	422	16.8	34	48	8	8
3	2.2	500	16.0	32	52	6	8
4	1.8	380	12.7	36	53	4	9
5	1.7	361	11.3	35	55	5	7
6	1.5	388	12.0	35	46	9	9
7	1.5	386	12.1	31	51	9	7
8	1.4	455	13.4	29	47	16	6

(b) PECVD SiN films.							
Sample	Temp. (°C)	Thickness (Å)	Dep. rate (Å/min)	Silicon (%)	Nitrogen (%)	Oxygen (%)	Hydrogen (%)
1	250.	2125	70.8	38	36	...	25
2	350.	1963	65.4	36	42	...	21

is then in competition with another reaction which involves oxygen since the RBS analysis shows a large amount of this element in our films. We have demonstrated previously that the oxygen content of the SiN film is directly dependent on the deposition rate for a fixed flux ratio.⁴ In Fig. 2 we have represented the oxygen and hydrogen contents of the MPCVD film versus the flux ratio. We can notice that the shape of the O-content curve is comparable to Fig. 1. Moreover the H-content curve is quasi-independent on the flux ratio. The oxygen content of the film appears then as a consequence of the deposition rate: the higher the deposition rate, the higher the O content.

A point which is up to now not elucidated, is the origin of the oxygen in our films. The gases which are introduced in the vessel are supposed to be quasi-free of water or oxygen. Nevertheless their residual oxygen concentration and the residual oxygen adsorbed on the walls of the chamber are certainly sufficient to provide the oxygen in our SiN films. This oxygen quantity is nevertheless very slow (under 0.01% if we take into account the static vacuum in the chamber and

the gases purity) compared with the nitrogen one. The great quantity of oxygen obtained in the films is certainly the result of the highest oxygen reactivity with silane. For CVD systems the silane decomposition mechanism is generally proposed to be the limitative step of the deposition rate.⁹ In our system the situation is more complex due to the occurrence of the oxygen and hydrogen species in the deposition process.

These different behaviors are confirmed by infrared absorption measurements. In Fig. 3 we have reported infrared absorption spectra of three dielectric films deposited on semi-insulating silicon: two MPCVD SiN films deposited at two different deposition rates (10 and 44 Å min⁻¹) obtained by varying the total pressure from 3.8 to 20 mTorr, keeping constant the flux ratio ($\text{SiH}_4/\text{N}_2 = 2.5\%$), and one PECVD SiN film deposited at 200 °C. The absorption peaks due to N—H stretching bonds and bending modes (3300–3400 cm⁻¹ and around 1200 cm⁻¹, respectively) are presented

FIG. 1. Deposition rate vs flux ratio for our MPCVD SiN films. The deposition rate is evaluated by spectroscopic ellipsometry.

FIG. 2. Oxygen and hydrogen content of MPCVD SiN films vs the flux ratio. O content is evaluated by RBS and H content by ERD (values provided in % of the total atomic content).

FIG. 3. Infrared absorption spectra of three different SiN films. The two MPCVD films have been performed at two different deposition rates (44 and 10 Å min⁻¹) changing only the total pressure (SiH₄/N₂ fixed at 2.5%), one PECVD film performed at 200 °C. The films have been deposited on semi-insulating silicon and the measurements have been corrected from the substrate absorption.

only on the MPCVD SiN film deposited at the higher deposition rate. On the contrary, the Si-H stretching mode (2150–2200 cm⁻¹)¹⁰ is only present in the PECVD film. If we assume that the hydrogen bonding in the films is repre-

sentative of the deposition mechanism, the specificity of our MPCVD system is confirmed. These very different behaviors are certainly related to the efficiencies of each type of plasma to ionize silane and nitrogen. A more detailed study is nevertheless necessary to precise the deposition mechanisms.

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