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Structural and electrical properties of silicon nitride films prepared by multipolar plasma-enhanced deposition

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A new system of dielectric deposition using a multipolar plasma enhanced by a hot filament has been used to deposit multipolar plasma chemical vapor deposition silicon nitride films on various substrates (GaAs, Si, GaInAs, etc.). Using *in situ* kinetic ellipsometry during the depositions, the flow ratio SiH_4/N_2 has been optimized to form as dense silicon nitride as possible. The density variation has been attributed to a variable amount of oxygen in the films certainly in the form of silicon dioxide. Using Rutherford backscattering and spectroscopic ellipsometry, the amounts of oxygen have been measured precisely. Using infrared absorption, we have demonstrated the low hydrogen concentration of our films compared to plasma-enhanced chemical vapor deposition ones. At constant flow ratio, we have demonstrated the effect of the deposition rate on the stoichiometry of the films. Films deposited at very low deposition rates ($< 10 \text{ Å/min}$) are quasistoichiometric and produce important reductions of GaInAs/ Si_3N_4 interface densities of states compared to higher deposition rate films ($> 24 \text{ Å/min}$). The conduction mechanism appears ionic in oxygen-rich silicon nitride films and controlled by a Poole-Frenkel effect in the case of moderate deposition rates.

I. INTRODUCTION

Amorphous 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 without plasma bombardment, and at low temperatures ($< 300^\circ\text{C}$).

For these reasons, new methods have been developed, like plasma-assisted chemical vapor deposition enhanced with rf discharges (PECVD),^{1,2} or more recently with microwave discharges,⁴ and systems based on light excitation (photo CVD).⁵

In this work, we use an ultrahigh vacuum system and a multipolar plasma described elsewhere.⁶ In a multipolar plasma source (which has a hot cathode associated with a magnetic confinement) homogeneous plasma in a large range of densities (10^8 – 10^{11} cm^{-3}) can be obtained in large volumes. Since its operation requires only modest dc voltages (below 75 V), the plasma is free from energetic particles. This type of plasma is used to perform multipolar plasma chemical vapor deposition (MPCVD) silicon nitride films in order to achieve a "good" electrical III-V semiconductor/ Si_3N_4 interface

This paper describes how physical properties of silicon nitride films change versus plasma conditions, and how these properties are related to the electrical behavior. Plasma-grown dielectric films have been controlled in real time by *in situ* kinetic ellipsometry. Physical properties of the films have been deduced from spectroscopic ellipsometry,

Rutherford backscattering, and infrared absorption measurements.

II. EXPERIMENT

A. Description of the multipole system

The multipole first used by Limpaecher and MacKenzie⁷ consists in an electron emitter (a hot filament) negatively biased (typically 20–100 V) with respect to the walls of a "magnetic" container. The primary electrons emitted by the hot emitter ionize the low-pressure gas admitted in the vessel.

Our multipole system is shown in Fig. 1. The emitted electrons are confined by permanent magnets mounted on the walls of the chamber. To adjust the characteristics of the plasma, we can change four parameters: (1) the filament potential; (2) the discharge current between filament and vessel (by varying the filament current heating); (3) the total pressure of the gas admitted in the vessel; (4) and the composition of the gas admitted in the vessel.

The sample holder is a quartz window and so the sample is electrically isolated in the plasma. This configuration ensures a minimum bombardment during the deposition. The heating is performed with infrared lamps, and the temperature is measured by a pyrometer ($T > 100^\circ\text{C}$). We use pure N_2 and SiH_4 diluted in hydrogen or argon ($\text{SiH}_4/\text{H}_2 = \text{SiH}_4/\text{Ar} = \frac{1}{3}$) as reactant gases. Flow meters allow one to control the composition of the plasma. The total pressure can vary from 1 to 20 mTorr.

B. *In situ* spectroscopic ellipsometer

A simplified schematical diagram of the experimental configuration is shown in Fig. 1. The ellipsometer is a photo-

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FIG. 1. Schematic view of the multipolar plasma chamber with the spectroscopic ellipsometer.

metric type related to Fourier-transform rotating-analyzer ellipsometers described previously.⁸ The main difference in the present configuration is that the source and detector are interchanged. The sequence of optical elements is a xenon lamp, a rotating polarizer, a sample, a fixed analyzer, a monochromator, and a photomultiplier. The selection of energy at the end of the sequence is essential, in the sense that all the parasitic lights are eliminated. This type of system has already been used to study plasma-grown GaAs oxides,⁹ or multilayer systems.¹⁰ Two types of measurements can be made. (1) A real-time measurement during deposition: in this case, the wavelength of the light is fixed and chosen to be sensitive to the expected phenomena. We use kinetic ellipsometry (KE). (2) Once a stable state is achieved, complementary information can be obtained by varying the wavelength. We then use spectroscopic ellipsometry (SE) in the range 1.6–5.4 eV.

C. Rutherford backscattering measurements

Rutherford backscattering measurements were performed with 2000-keV He^+ particles, produced by a 2500-kV Van de Graaff accelerator. Backscattered He^+ ions were measured with an Ortec surface barrier detector at a scattering angle of 170° . The energy resolution of the detection system was measured to be 13 keV full width at half maximum (FWHM), in this configuration corresponding to a depth resolution of ≈ 200 Å. Using this resolution, no variations in composition as a function of depth were found. In order to separate the relatively small N, O, and Si signals from the GaAs background, channeling was applied. The peak areas of N, O, and Si signals were obtained by subtracting a third-order polynomial fit through the GaAs background and were converted into the number of atoms/cm² using the procedure given by Ziegler.¹¹

D. Infrared absorption

Infrared absorption measurements were made in transmission using a Perkin Elmer 983 system. For this study, films are deposited on low-doped silicon wafers to minimize the substrate absorption (doping $< 10^{15} \text{ cm}^{-3}$). In fact, we measure the absorption spectra (in the range 200–4000 cm^{-1}) of the sample before and after deposition, and we make the difference to obtain the contribution of the silicon nitride film alone.

E. Samples and electrical characterization

The leakage currents of the dielectric films are measured on highly doped substrates (GaAs or Si), using a picoammeter HP4140B in a system where the temperature of the sample can be changed from 100 to 400 K. To test the influence of the deposition conditions of the films on interface states, we have deposited Si_3N_4 on GaInAs layers epitaxially grown on highly doped n -type InP substrates by the chloride method. The n -type GaInAs layers are unintentionally doped with a residual carrier concentration of about 10^{15} cm^{-3} . They are only degreased in solvents and chemically cleaned in diluted HF prior to the insulator deposition in order to avoid a large amount of oxide on the surface. After 1-h annealing at 400°C under argon, the metal-insulator-semiconductor (MIS) structure is completed by an evaporation of Ti and Au through a metal mask. A post-metalization annealing is finally performed at 400°C for 15 min to suppress the radiation damages induced by the metalization. $C(V)$ curves are measured at 1 MHz by a HP4192A impedance analyzer and the density of interface states is evaluated by Terman's method.²⁰

III. STRUCTURAL PROPERTIES OF SILICON NITRIDE FILMS

A. Effect of silane/nitrogen ratio on silicon nitride stoichiometry

1. *In situ* kinetic ellipsometry

As mentioned before, it is possible to change four parameters of the multipolar plasma. We first adjusted the ratio $R = \text{SiH}_4/\text{N}_2$ of flow gases introduced in the vessel because the optical characteristics of the films vary drastically with this parameter. This observation is illustrated in Fig. 2 where we report KE measurements performed *in situ* at 4 eV, during three experiments on GaAs substrates, changing only the ratio R from 4.2% to 2.5%. We observe that the slope $d\Delta/d\psi$ changes in the three depositions, indicating a change of the dielectric constants of the films. In fact, not

FIG. 2. Kinetic ellipsometry trajectories measured at 4 eV during three different multipolar plasma depositions of Si_3N_4 on GaAs varying only the gas flowrate SiH_4/N_2 .

FIG. 3. Temporal evolution of the two ellipsometric parameters ψ and Δ during the three depositions described previously (cf. Fig. 2).

only do the trajectories vary but the deposition rates vary as well, as is clearly seen in Fig. 3 where we report the temporal evolution of the two ellipsometric parameters Δ and ψ . The deposition rate drastically decreases when we reduce the ratio R (and thus the quantity of SiH_4), and seems to saturate for ratios lower than 2%. To explain these results it is necessary to obtain chemical information with other experimental techniques.

2. Rutherford backscattering results

In all the analyzed samples we notice the existence of oxygen atoms in the films, but in variable amounts. The results of these analyses are summarized in Table I, not only for the three previous rates R but also for different conditions of deposition discussed later (temperature, gas dilution

FIG. 4. Theoretical modeling of the dielectric deposition varying film thickness and SiO_2 percentage in stoichiometric Si_3N_4 . The three previous experimental trajectories (cf. Fig. 2) are also reported.

of silane, etc.). The amounts of oxygen increase from 8% for $R = 2.5\%$ to 24% for $R = 4.2\%$.

If we assume that the oxygen is linked with silicon atoms in order to create Si-O bonds, we can simulate KE trajectories by modeling the deposited films with a mixture of pure reference materials Si_3N_4 and SiO_2 , using the effective medium average.¹² Such simulation is shown in Fig. 4 where experimental KE trajectories (cf. Fig. 2) are superposed on theoretical trajectories evaluated with varying film thickness and SiO_2 percentage in stoichiometric Si_3N_4 . We can see that the increase of R corresponds to an increase of the amount of SiO_2 in agreement with RBS results (cf. Table I). The concentrations of SiO_2 deduced from KE measurements are unfortunately not very accurate because the initial states of the

TABLE I. Plasma conditions and physical characteristics of dielectric films deposited on GaAs and Si substrates. Both SiH_4/N_2 ratio, substrate temperature (unh. means unheated), and discharge current have been changed in the deposition plasma. The number of deposited atoms per cm^2 have been measured by Rutherford backscattering (RBS), and insulator thickness and compositions have been deduced from spectroscopic ellipsometry.

Sample	1 GaAs	2 GaAs	3 GaAs	4 GaAs	5 GaAs	6 GaAs	7 GaAs	8 Si
Plasma conditions								
Temp. (°C)	unh.	unh.	200	unh.	220	220	unh.	unh.
I (mA)	105	185	105	185	1000	100	60	185
SiH_4/N_2	2.5	2.8	2.5	4	4	4	4.2	2.8
RBS results								
Si 10^{16} atoms/ cm^2	17.2	19.1	9.2	14.7	20.8	8.9	13.0	22.2
N 10^{16} atoms/ cm^2	26.5	25.0	15.4	20.5	28.4	13.2	16.8	21.9
O 10^{16} atoms/ cm^2	3.5	10.9	1.2	2.7	2.6	3.5	9.7	7.5
O (%)	7.4	19.8	4.6	7.1	5.0	13.7	24.5	14.5
Si + N + O (%)								
Ellipsometry results								
Insul. thick. (Å)	542	740	355	620	800	427	633	730
(%) of SiO_2	24.5	44.7	11.1	22.8	15.0	24.5	43.7	42.0
O (%)	8.1	17.1	3.4	7.5	4.7	8.1	24.3	15.8
Si + N + O (%)								

different samples on which we performed the depositions are not exactly the same. To improve these results it is necessary to use SE measurements realized before and after deposition.

3. Correlation Rutherford backscattering/spectroscopic ellipsometry

For all the deposited films, we have made a SE measurement just before and after the deposition. The initial state is modeled assuming the existence of thick native oxide on the substrate (GaAs or Si). The parameters of this model (oxide thickness and incident angle which depends on the ellipsometer alignment) are then determined by linear regression analysis (LRA),¹³ which minimizes the error function F given by

$$F = \sum_E |\tan \psi(E)_{\text{cal}} - \tan \psi(E)_{\text{exp}}|^2 + \sum_E |\cos \Delta(E)_{\text{cal}} - \cos \Delta(E)_{\text{exp}}|^2.$$

The SE measurement after deposition is then modeled assuming the existence of the native oxide thickness previously determined under a mixture of $(\text{Si}_3\text{N}_4)_{1-x}(\text{SiO}_2)_x$. Thickness and composition x of this deposited layer obtained by the same method are summarized in the Table I.

The agreement between RBS and SE results can be evaluated by the use of the oxygen ratio in terms of the relative number of atoms per cm^{-3} . This ratio is directly determined from RBS measurements, and evaluated from the SE results, taking into account the ideal compositions of the two reference materials of the model. The correspondence is illustrated in Fig. 5 including the standard deviations of the two techniques. The correlation is nearly perfect except on one sample (unfortunately, the thickness of the films produces a great resonance in this case, disturbing SE measurements). Keeping R constant at 2.5%, we tried to clarify the role of the temperature and of the deposition rate.

B. Effect of temperature on silicon nitride stoichiometry

We made some depositions heating the substrate up to 300 °C during the plasma (temperature which is still accep-

FIG. 5. Correlation between oxygen amounts determined in various samples by Rutherford backscattering and spectroscopic ellipsometry. The standard deviations of the two techniques are also reported.

FIG. 6. Kinetic ellipsometry trajectories measured at 4 eV during two different multipolar plasma depositions of Si_3N_4 on GaAs varying only the temperature of the sample during the plasma. Theoretical modelization of the dielectric deposition is made varying the thickness of a stoichiometric Si_3N_4 layer.

table for post-encapsulation technologies). In Fig. 6, we report two KE measurements performed *in situ* at 4 eV, during two different film depositions on GaAs substrates. The ratio R has been kept constant at 2.5%, and we only heated the substrate up to 200 °C before the deposition in the second case. The effect of the temperature on KE trajectories on GaAs has been previously determined¹⁴ in terms of variations of dielectric constants of the substrate. The parallelism of the two KE trajectories during the deposition is in fact characteristic of the same stoichiometry of the film. This result is in agreement with SE results and RBS results (cf. Table I). On the other hand, the deposition rate is reduced in this case from 3 to 2 Å/min by the heating. This effect of temperature on Si_3N_4 deposition rate is not surprising since it has been noticed with other methods of deposition like PECVD.¹

C. Effect of deposition rate on silicon nitride stoichiometry

1. Spectroscopic ellipsometry measurements

Keeping the R ratio constant (at 2.5%), we changed the deposition rate by varying the total pressure and the discharge current of the plasma. Thickness and stoichiometry of the silicon nitride films have been evaluated by SE measurements in terms of percentage of SiO_2 in Si_3N_4 . In Fig. 7 we have reported some results obtained for deposition performed on GaInAs samples. The great dependence of the film stoichiometry versus deposition rate is obvious. We also noticed that the same plasma conditions ($I = 105$ mA, $P = 6.5$ mTorr, for example) do not provide exactly the

same silicon nitride films. This must be related to the initial state of the surface before the deposition which is different in both cases (varying the chemical treatment, or performing an *in situ* native oxide removal by a H_2 plasma¹⁵). The amount of oxygen at the surface before deposition seems to influence the quality of the film (lower deposition rates and more stoichiometric silicon nitride films are systematically obtained on clean surfaces). The same type of behavior has been noticed on Al_2O_3 films performed on InP surfaces.¹⁶

2. Infrared absorption results

Typical infrared absorption spectra ranging from 200 to 4000 cm^{-1} are displayed in Fig. 8. We can compare our optimized silicon nitride films with a "classical" PECVD silicon nitride film performed at 200°C . The absorption peaks due to N-H stretching bonds and bending modes ($3300\text{--}3400\text{ cm}^{-1}$ and around 1200 cm^{-1} , respectively) and to Si-H stretching mode ($2150\text{--}2200\text{ cm}^{-1}$)¹⁷ are present only in the PECVD film. The accuracy of the IR absorption measurement is about 0.5%, then the detection limit for the hydrogen content can be evaluated to a few atomic percent for our silicon nitride thickness. It means that our films are nearly free of hydrogen compared to typical PECVD layers [$\approx 20\%$ (Ref. 18)]. In contrast, the position of the absorption peak corresponding to a Si-N stretching mode (around 850 cm^{-1}) seems to be shifted to lower values. This behavior is most probably due to the occurrence of another peak corresponding to a Si-O stretching mode.

Since the absorption spectra reported previously are characteristic of a slow deposition rate ($3\text{ \AA}/\text{min}$), it would be interesting to try to emphasize the effect of the deposition rate on the stoichiometry of the film by this method. In Fig. 9, we have reported the absorption spectra of three films realized with different deposition rates (from 10 to $44\text{ \AA}/\text{min}$). When the deposition rate is increased, we first notice that the two absorption peaks corresponding to N-H bonds appear, and second, observe that the position of the maximum of the Si-N absorption peak is shifted to the higher wavelength numbers. This second observation can be used to have an idea of the stoichiometry of the silicon nitride film.

FIG. 7. Oxygen amounts determined by spectroscopic ellipsometry in dielectric films performed with different deposition rates obtained by changing both discharge current or total pressure of the multipolar plasma.

FIG. 8. Infrared absorption spectra of two dielectric films: one performed at 200°C in a PECVD system ($\approx 1000\text{ \AA}$) and the other in our system at room temperature with optimized plasma conditions ($\approx 470\text{ \AA}$). The theoretical positions of the different absorption peaks are also reported.

In Fig. 10, we have reported this absorption peak position for all the films which have been examined by SE previously (cf. Fig. 7) versus the percentage of SiO_2 in the film. The correlation between these two types of results is quite good in spite of a poor accuracy in the position of the maxima of the absorption peak ($< 10\text{ cm}^{-1}$).

IV. ELECTRICAL PROPERTIES OF SILICON NITRIDE FILMS

A. Conduction mechanism in the silicon nitride

Resistivity, breakdown field, and dielectric constant of an insulating film often depend on the fabrication conditions. These values have been determined for films deposited at various rates and hence with different compositions as described earlier.

Except for the sample which contains the highest concentration of oxygen where the resistivity at $1\text{ MV}/\text{cm}$ can vary from 2×10^{11} to $5 \times 10^{13}\text{ }\Omega\text{ cm}$, other samples have a resistivity of approximately $5 \times 10^{13}\text{--}2 \times 10^{14}\text{ }\Omega\text{ cm}$. The breakdown field is always around $5 \times 10^6\text{ V}/\text{cm}$. The dielectric constants ϵ_r have been evaluated from the capacitance in the accumulation region for various frequencies. In Table II we summarized the data for the three deposition rates. At 1

FIG. 9. Infrared absorption spectra of three different dielectric films performed at three different deposition rates ($10\text{--}44\text{ \AA}/\text{min}$). The positions of the three absorption maxima are also reported. The film thicknesses are of the order $\approx 470\text{ \AA}$.

FIG. 10. Energy position of the maximum absorption peak (Si-N and Si-O bonds) for various infrared absorption spectra obtained on different dielectric films varying the deposition rate (measured by spectroscopic ellipsometry).

MHz, ϵ_i varies from 6.3 to 7.2 versus deposition conditions and its frequency dispersion is rather low in all samples compared to other silicon nitrides.³

To determine the conduction mechanism, current density (J) has been measured versus applied field (E) at room temperature and then versus temperature at a fixed applied field. The most probable mechanism has then been identified by comparing the $J(E)$ curves with the predictions of established mechanisms.¹⁹ $J(T)$ measurements allow one to know the activation of the mechanism process.

Figures 11(a) and 11(b) show the current density J vs E and $\sqrt{E}$, respectively, for two different silicon nitride films. For the highest deposition rate, the current density is high and proportional to E . Two mechanisms can explain this dependence; either it is ohmic or ionic. If the conduction is ionic, an hysteresis must occur on the $I(V)$ curves. As can be seen in Fig. 12, an hysteresis exists and probably the dielectric contains ions. From the temperature dependence (Fig. 13), it seems that the current density is governed by a distribution of traps and it is not possible to determine an activation energy. This behavior is a consequence of bad quality silicon nitride film in terms of stoichiometry and oxygen concentrations.

In the case of a moderate deposition rate (24 Å/min), at high electric field, the linear region can be modeled by the following expression:

$$J = A^* T^2 \exp - q \left[\left(\phi_B - \sqrt{qE/n\pi\epsilon_0\epsilon_i} \right) / kT \right],$$

FIG. 11. (a) Current density J vs electric field E for silicon nitride films deposited at 24 and 44 Å/min. (b) Current density J vs electric field $\sqrt{E}$ for silicon nitride films deposited at 22 and 44 Å/min.

TABLE II. Electrical characteristics of three dielectric films deposited on GaInAs at different deposition rates (44, 24, and 10 Å/min).

Sample	Deposition rate (Å/min)	ρ (Ω cm)	E_B (V/cm)	ϵ at 1 MHz	ϵ at 500 Hz	$\Delta\epsilon$
1	44	1.6×10^{11} to 5×10^{13}	5.2×10^6	6.34	6.58	0.24
2	24	4×10^{13}	4×10^6	7.20	7.67	0.47
3	10	3×10^{13} to 2×10^{14}	4×10^6	6.8	7.0	0.20

FIG. 12. $I(E)$ curve for silicon nitride deposited at 44 Å/min . An hysteresis exists in this case. In the inset is shown the $I(V)$ curve corresponding to the deposition rate of 24 Å/min ; no hysteresis occurs for the same electric field.

where A^* is the effective Richardson constant, q is the electronic charge, ϕ_B is the barrier height, ϵ_i is the dielectric constant and n is a constant with the value 1 or 4. If $n = 1$, this law describes a Poole-Frenkel (bulk) mechanism and for $n = 4$, the mechanism is a Schottky (interface controlled) emission. From the slope of the $I(\sqrt{E})$ curve, we can determine ϵ_i , and by comparison with the dielectric constant evaluated from the $C(V)$ measurements, the mechanism can be identified. The experimental data give $\epsilon_i = 7.06$

FIG. 13. Temperature dependence of the current density for the silicon nitride film deposited at 44 Å/min . $\log(J \cdot T)$ is represented vs $1/T$.

FIG. 14. Temperature dependence of the current density for silicon nitride films deposited at 24 and at 44 Å/min . $\log(J)$ is represented vs $1/T$.

and 1.76 if we assume, respectively, a Poole-Frenkel mechanism and a Schottky emission. For the moderate deposition rates, the conduction in the silicon nitride is governed by traps located in the bulk of the insulator.

From the dependence of $\log(J)$ vs $1/T$, the energy ϕ_B required to ionize the charge carrier from the trap can be calculated. In Fig. 14, we can notice a tunneling mechanism at low temperatures (J independent of T from 100 to 250 K) and activated processes whose activation energies have been evaluated to 0.73 and 1.24 eV, respectively.

B. GaInAs interface states density and silicon nitride stoichiometry

MIS structures have been fabricated on GaInAs samples covered with silicon nitride films realized with three

FIG. 15. (a) 1-MHz capacitance normalized to the insulator capacitance C_i vs voltage for MIS structures on GaInAs using silicon nitride deposited at 10, 24, and 44 Å/min . (b) 1-MHz conductance divided by $C_i \omega$ vs voltage for the same samples as described in (a).

FIG. 16. Distribution of the interface states density deduced by Terman's method from the 1 MHz $C(V)$ curves for MIS structures on GaInAs using silicon nitride deposited at 10, 24, and 44 Å/min.

different deposition rates (10, 24, and 44 Å/min) corresponding to samples prepared at the same time as the silicon ones described previously (cf. Fig. 9).

Capacitance and conductance at 1 MHz have been measured versus voltage and the normalized values are represented in Figs. 15(a) and 15(b), respectively. The modulation of the capacitance is considerably reduced in the case of the highest deposition rate and the conductance is rather high, especially since it does not present a maximum in the depletion region which indicates a high density of traps. For the intermediate deposition rate the modulation of capacitance increases but the capacitance does not show a plateau at negative voltages which indicates, together with the conductance in this region, that inversion is not reached. On the contrary, for the lowest deposition rate, at negative voltages the capacitance curve shows a plateau and the conductance decreases to the same value as in the accumulation region, showing that inversion is reached.

The interface state density has been deduced from these high-frequency $C(V)$ curves using Terman's method²⁰ and results represented in Fig. 16 show that density of traps at the interface decreases when the deposition rate becomes lower.

N_{ss} decreases from 2×10^{13} to 2.5×10^{12} cm⁻² eV⁻¹ when the deposition rate varies from 44 to 10 Å/min. At the same time, the modulation of the surface potential increases from 0.1 to 0.5 eV.

As deduced from RBS and SE experiments the increase of deposition rate corresponds to silicon nitrides further from stoichiometric ones. Hence, the electrical behavior of the silicon nitride/GaInAs interface strongly depends on the composition of the dielectric film. The lower the concentration of oxygen is, the better are the electrical properties of the interface because the density of traps in the insulator itself and at the interface is lower.

V. DISCUSSION AND CONCLUSION

We have demonstrated the possibility of depositing quasi-stoichiometric MPCVD silicon nitride films using a SiH₄ + N₂ multipolar plasma enhanced by a hot filament.

The potentialities of an ellipsometer *in situ* on the multipolar plasma chamber have been used to optimize the flux ratio SiH₄/N₂ and the deposition rate. The optimized conditions (SiH₄/N₂ = 2.5% and the deposition rate under 10 Å/min) provide films quasi-free of hydrogen and with oxygen concentrations under 5%. The incorporation of hydrogen in the film becomes efficient when the deposition rate is increased up to 40 Å/min but only in the form of N-H bonds (cf. Fig. 8). This hydrogen behavior is completely different than what is generally noticed in PECVD film, that is, the hydrogen generally appears bonded with silicon. This fact is certainly to be related to the high efficiency of a hot filament to decompose silane compared to nitrogen. The great excess of nitrogen necessary to deposit stoichiometric silicon nitride clearly demonstrates this assumption. To our knowledge, it is the first low-temperature deposition method using silane that is able to deposit silicon nitride films quasi-free of hydrogen (hydrogen-free Si₃N₄ films have recently been achieved by ion beam sputtering using a Si target, but the degradation due to the bombardment by high-energy ions is still a problem in this type of technique²¹).

Unfortunately, in our system the main contaminant is oxygen, which has a great effect both on the electrical properties of the silicon nitride and on the interface density of states in the case of GaInAs. Because of the ultrahigh vacuum atmosphere and the occurrence of a load lock chamber to introduce samples, the oxygen is certainly introduced in the plasma chamber with the reactant gases. This oxygen certainly has a great role during the growing of the silicon nitride films. The occurrence of an excess of oxygen at the surface of the sample (in the form of native oxide) before the deposition has an effect on the growing of all the film. On a clean surface (obtained by using a H₂ plasma, for example¹⁵) the deposition rate is lower than on an oxidized one, and the amount of oxygen in all the thickness of the film is reduced. Nevertheless, in some cases where the homogeneity of the deposit is an important parameter (post-encapsulation of integrated circuits on GaAs, etc.), the occurrence of a low amount of oxygen in the films can have a beneficial effect because an oxynitride is generally less stressed than a pure silicon nitride.^{14,22}

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