Extended Abstracts of the 18th (1986 International) Conference on Solid State Devices and Materials, Tokyo, 1986, pp. 245-248



# Variation of Electrical and Optical Properties of Glow Discharge Si-N-H Films with Their Composition

Nicole PROUST, François BOULITROP , Bernard HEPP, Nicolas SZYDLO, Eric CRITON and José MAGARINO

THOMSON-CSF

Central Research Laboratory, BP N°10,
91401 ORSAY Cedex, FRANCE

Abstract : Silicon nitride films are prepared by 13,56 MHz glow discharge of $SiH_4$-$NH_3$ mixtures Electrical measurements, XPS, IR spectroscopy, optical transmission and PDS are used to optimize Si-N-H as a TFT gate insulator. It is found that the highest critical field is obtained when the films exhibit particular densities of H bound to N and Si and when the stoechiometric N/Si ratio is achieved.

## I - Introduction

Silicon nitride films prepared by glow discharge system have been widely used in modern semiconductor processes : as a final encapsulation film for integrated circuit chips[1)2)] and recently as a-Si:H TFTs' gate insulator for active matrix liquid crystal displays[3)4)5)6)]. Silicon nitride films can be deposited either from $SiH_4$ -$NH_3$[7)8)9)] or $SiH_4$-$N_2$ mixtures[10)11)12)13)]. In the present study Si-N-H films are prepared by 13.56 MHz glow discharge of $SiH_4$-$NH_3$. The film properties have been analysed by I, V measurements, XPS, IR spectroscopy, optical transmission and PDS experiments in order to determine the optimum deposition parameters to get the best Si-N-H for gate insulator and for passivation layer.

## II - Experimental

We have used for deposition a traditional planar cold wall 13.56 MHz glow discharge reactor designed and fabricated by SOLEMS for large size (8" x 8") a-Si:H solar cell applications. A schematic view of the stainless steel reaction chamber is shown on figure 1. The $SiH_4$ -$NH_3$ (total gas flow : 25 sccm) mixture is introduced in the chamber by diffusion, it is evacuated by a pumping group composed by a diffusion pump, a roots and a rotary pump. The typical deposition procedure is as follows : chemically etched substrates of fused silica or of monocrystalline Si are put on the substrate holder. The system is pumped down to $10^{-6}$ mTorr. When the deposition temperature is reached the active gases are introduced in the chamber. The RF power is switched on only when the deposition pressure is stabilized. After deposition the reactor is pumped down and refilled with nitrogen. The substrates are then unloaded.

The deposition parameters used in this study are :

$T_D$ = 200°C to 350°C
$P_D$ = 30 mTorr, 80 mTorr
$P_W$ = 15 watts, 20 watts, 25 watts
R = $SiH_4/(NH_3 + SiH_4)$ from 8% to 30%.

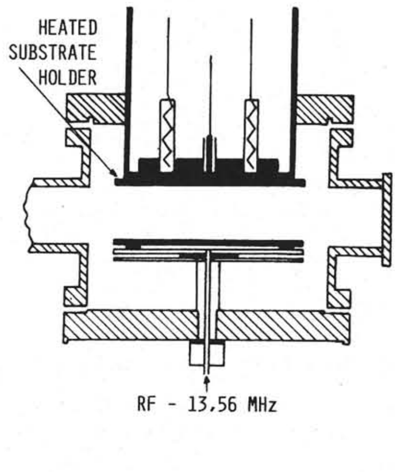


Fig. 1 Reaction chamber.

### III - Electrical measurements

Quasi-static I-V measurements are performed at $5 \times 10^{-4}$ Hz on thin Si-N-H films deposited on n-type crystalline silicon substrates. Small aluminium dots (600 $\mu$m diameter) are evaporated on the nitride to obtain individual capacitors. The capacitor leakage current is measured by applying a positive bias up to 50V. The critical field $E_C$ is obtained at the value of the electric field corresponding to a leakage current density of $\Delta J = 2 \times 10^{-10} Acm^{-2}$. Results are reported on figures 2-3 and 4 for different deposition conditions. Figure 2 is relative to nitrides prepared at 250°C under a pressure of 30 mTorr and RF powers of 15watts and 25 watts, $E_C$ is almost independent of the RF power and depends on the gas phase composition R. $1,7 \times 10^6 Vcm^{-1} < E_C < 2 \times 10^6 Vcm^{-1}$. On figure 3 for films deposited at 250°C under a total pressure of 80mTorr at 15 watts and 25 watts, $E_C$ depends on both RF power and gas composition R. The highest $E_C$ ( $\sim 3 \times 10^6 Vcm^{-1}$) is obtained for 80 mTorr and 15 watts. Figure 4 represents $E_C$ as a function of the refractive index for films prepared at temperatures of 200°C and 350°C at 30 mTorr and 20 watts. A higher $E_C$ is obtained at 350°C ($2.3 \times 10^6 Vcm^{-1}$) than at 200°C ($1.3 \times 10^6 Vcm^{-1}$). The refractive index shift for $E_C$ max is mainly due to the hydrogen content.

In summary the highest critical fields are obtained when the RF power is low (15W), the pressure high (80mTorr) and the temperature the highest (350°C).

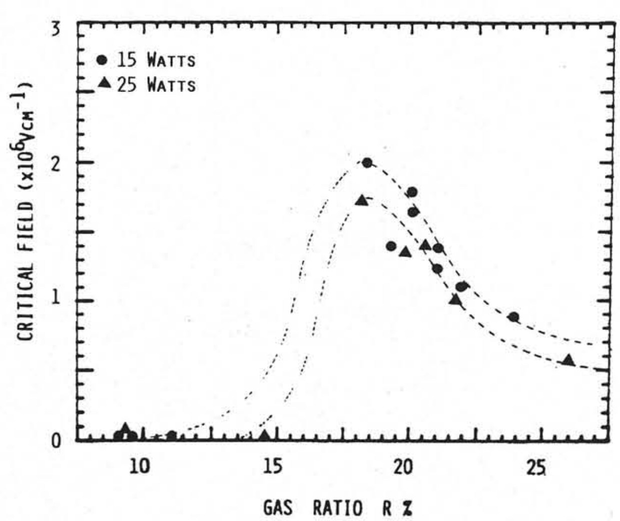


Fig. 2 Critical field as a function of gas phase composition at $P_D$ = 30 mTorr.

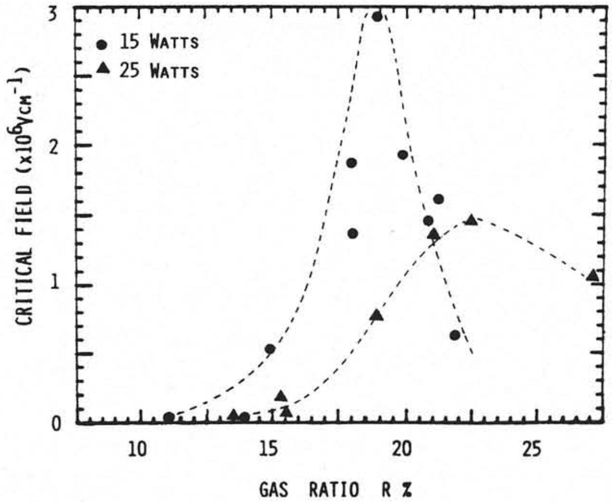


Fig. 3 Critical field as a function of gas phase composition at $P_D$ = 80 mTorr.

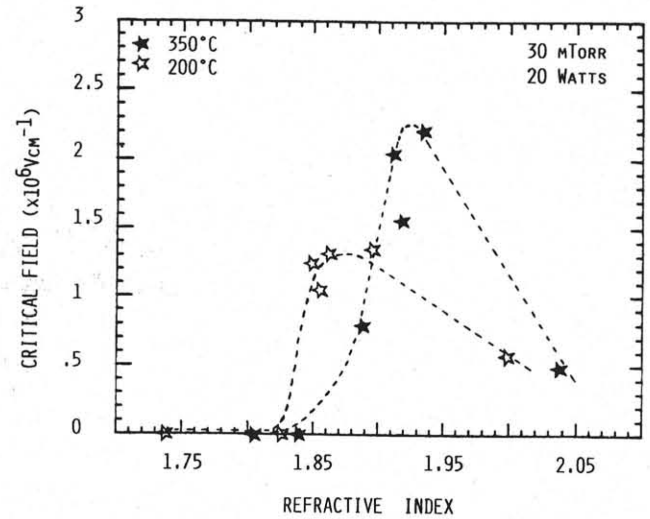


Fig. 4 Critical field as a function on the index of refraction at $T_D$ = 350°C and 200°C.

### IV - XPS experiments

Stoechiometry has been investigated on thin and thick Si-N-H films. The N/Si ratio is measured as a function of gas phase composition R. As R is increased, N/Si is decreased which is consistent with the refractive index variation with R. No significant variation of N/Si is observed when XPS analysis is done at various depth on the same sample.

Correlation between critical field measurements and N/Si ratio indicates that the samples with the highest $E_C$ present N/Si ratio between 1.4 and 1.2 which is not far from the stoechiometric ratio.

### V - IR experiments

Si-N-H films (5000 Å to 8000 Å) are deposited on thick Si substrates with both faces polished in order to perform infrared transmission measurements.The intensity of Si-H at 2150 $cm^{-1}$ and N-H at $3350 cm^{-1}$ stretching mode absorption peaks are studied as the gas phase composition is changed. On figure 5 we have reported IR results for samples prepared under the following conditions : 200°C, 20 watts, 30 mTorr, 14% < R < 25%. At low R we have only N-H peak, if R is increased the Si-H peak appears too, at high R most of the hydrogen is bound to Si.

The density of H bound to N or Si is given by $A\int\frac{\alpha(\omega)}{\omega}d\omega$. It is difficult to know the exact density of H bound to Si and to N as a lot of different values[14)15)16)] are available for $A_{Si-H}$ and $A_{N-H}$, but $\int\frac{\alpha(\omega)}{\omega}d\omega = S$, directly calculated from the absorption peaks is really representative of Si-N-H films.

We have compared the different values of S obtained at $2150 cm^{-1}$ and $3350 cm^{-1}$ for the samples prepared at 250°C and 310°C, 30 mTorr, 20 watts which present the highest critical field. At 250°C, $S_{N-H} \sim S_{Si-H} = 80 cm^{-1}$ and at 310°C, $S_{NH} \sim S_{Si-H} = 60 cm^{-1}$.

In conclusion when we have the highest critical field, the stoechiometric N/Si ratio is approximatly achieved and particular density of H is bound to N and to Si in our samples as $S_{N-H} \sim S_{Si-H}$. Taking $A_{N-H} = 1.5\times10^{20} cm^{-2}$, $A_{Si-H} = 1\pm0.2\times10^{20} cm^{-2}$)[17)] and Si-N atomic density = $8\times10^{22} cm^{-3}$ the total hydrogen content can be estimated and is found to change from ∿ 25% at 200°C to ∿ 13% at 350°C.

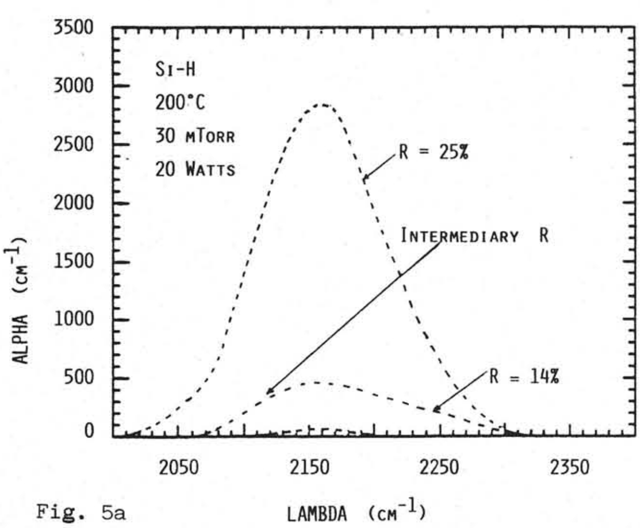


Fig. 5a

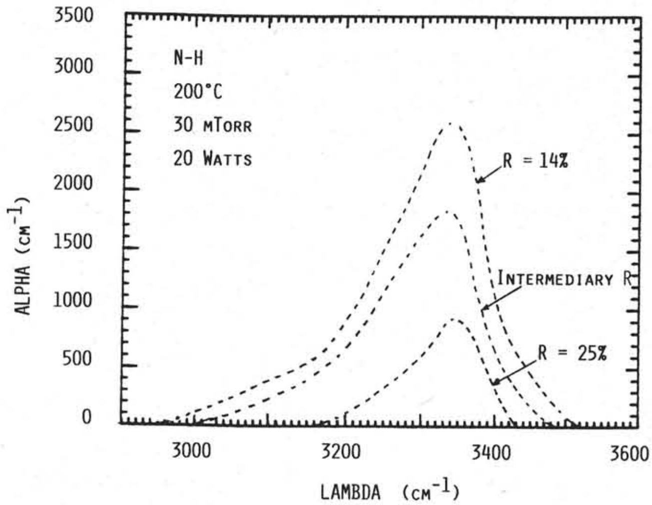


Fig. 5b

Fig. 5 IR absorption peaks for Si-H (5a) and N-H (5b).

### VI - Optical absorption

Important information on electronic states an particularly sub-gap states in amorphous semiconductors and insulators can be obtained by optical measurements of visible and UV light. Standard transmission is commonly used to estimate the absorption coefficient $\alpha$ . The value of the optical gap Eg is then inferred from a Tauc-plot. However, only high absorption coefficients ($\alpha > 10^2 cm^{-1}$ for 1μm thick films) are obtained accurately. To achieve a precise measurement of sub-gap optical absorption we performed Photothermal Deflection Spectroscopy (PDS). This technique has been successful in investigating valence band tail states and deep gap states in a-Si:H[18)], since absorption coefficients lower than $1 cm^{-1}$ can be measured without any physical unverified assumption. Details on the experimental set-up have been described elsewhere[19].

A series of Si-N-H films (∿ 5000 Å) have been deposited on fused silica substrates which show no absorption in the energy range of interest. Deposition parameters are : $T_D$ = 250°C, $P_D$ = 30 mTorr, $P_W$ = 15W and R from 15% to 21,5%.

Transmission and PDS measurements were performed for photon energies from 1.5 to 6 eV. The absolute values of $\alpha$ deduced from PDS have been adjusted for each spectrum to fit $\alpha$ values obtained by transmission in the region where both techniques are accurate.

The absorption spectra (fig. 6) show an exponential decrease in the region below the gap, which is commonly observed in other amorphous materials. The value of the slope $E_o$ of the exponential decrease and the optical gap $E_G$ are listed in the following table.

| $R=SiH_4/(SiH_4+NH_3)$ | $E_G$(eV) | $E_O$(meV) |
|---|---|---|
| 21.5 | 4.4 | 200 |
| 20.6 | 4.6 | 370 |
| 17.5 | 5.1 | 470 |
| 15 | 5.2 | 525 |

We observe an increase of both parameters when the silane content in the gas phase decreases. However, $E_o$ exhibits a strong variation in the quasi stoechiometric region indicating a strong enhancement of disorder for N-rich films. Further investigations should permit to correlate this particular point with electrical properties.

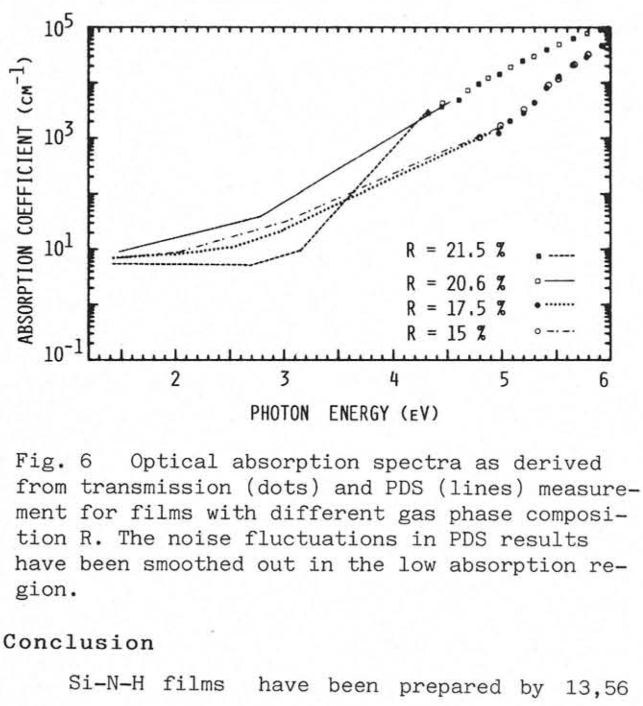


Fig. 6 Optical absorption spectra as derived from transmission (dots) and PDS (lines) measurement for films with different gas phase composition R. The noise fluctuations in PDS results have been smoothed out in the low absorption region.

## Conclusion

Si-N-H films have been prepared by 13,56 MHz glow discharge of $SiH_4$-$NH_3$ mixtures. Electrical measurements, XPS, IR spectroscopy, optical transmission and PDS are used to determine the most suitable nitride for TFT gate insulator and passivation layer. It is found that the critical field $E_C$ depends mainly on pressure, gas phase composition and temperature. $E_C$ is high when power is low (15W), pressure is high (80 mTorr), temperature ranges from 250°C to 350°C and R ranges from 17% to 25%. The highest $E_C$ is obtained when the films exhibit particular densities of H bound to N and Si ($S_{N-H} \sim S_{Si-H}$) and when the stoechiometric N/Si ratio is achieved.


## Acknowledgement

We are grateful to Drs. A. Deneuville and E. Bustarret for helpful information and discussion.

This work has been partially supported by EEC under ESPRIT program n° 833.


## References


1) J.G. Tenedorio and P.A. Terzian, IEEE Electron Device Letters, Vol. EDL5, n°6, p 199 (1984)
2) C.E. Morosanu, Thin Solid Films, 65, p 171 (1980).
3) M. Yamano, H. Takesada, M. Yamasaki, Y. Okita and H. Hada, IEEE Trans. Consumer Elect. CE 31, 39 (1985).
4) T. Yanagisawa et al., Proc. 4th Int. Display Res. Conf., Paris (S.E.E., Paris, 1984) p 265.
5) T. Sunata et al., Conf. Record. 1985, Int. Display Res. Conf. (IEEE, New York 1985) p 66.
6) Product announcement : "Panasonic Pocket Watch", Matsushita Electric Corporation of America, 1/86.
7) A.K. Sinha, H.J. Levinstein, T.E. Smith, G. Quintana, and S.E. Haszko, Electrochem. Soc. Vol 125, N°4, p 601 (1978)
8) A.C. Adams, Solid State Technology, p 137 (1983)
9) S. Yokoyama, N. Kajihara, M. Hirose and Y. Osaka, T. Yoshimara and H. Abe, J. Appl. Phys. Vol 51, n° 10, p 5470 (1983)
10) Y. Kuwano, Jap. J. Appl. Phys., Vol. 8, n° 7, p 876 (1969)
11) S. Fujita, N.S. Shou, and A. Sasaki, Jap. J. Appl. Phys. Vol 22, n° 2, p L100 (1983)
12) K. Katoh, M. Yasui and H. Watanabe, Jap. J. Appl. Phys. Vol 22, n° 5, p L321 (1983)
13) H. Dun, P. Pan, F.R. White and R.W. Douse, J. Electrochem. Soc, Vol 128, N° 7, p 1557 (1983)
14) V.J. Kapoor, R.S. Bailey and H.J. Stein, J. Vac. Sci. Technol. A.1 (1983)
15) T. Makino, J. Electrochem. Soc., Vol 130, p 450 (1983)
16) W.A. Lanford, M.J. Rand, J. Appl. Phys. Vol. 49, n° 4, p 2473 (1978)
17) - C. Chaussat, E. Bustarret, J.C. Bruyere, R. Crosleau, Physica B, Vol 129, p 215 (1985)
   - E. Bustarret to be published.
18) W.B. Jackson and N.M. Amer, Phys. Rev. B, Vol 25, n° 8, p 5559 (1982)
19) F. Boulitrop, J. Bullot, M. Gauthier, M.P. Schmidt and Y. Catherine, Solid State Com. Vol. 54, n°1, p 107 (1985)