



HAL
open science

CHARACTERIZATION OF INTRINSIC STRESSES OF PECVD SILICON NITRIDE FILMS DEPOSITED IN A HOT-WALL REACTOR

K. Aite, R. Koekoek, J. Holleman, J. Middelhoek

► **To cite this version:**

K. Aite, R. Koekoek, J. Holleman, J. Middelhoek. CHARACTERIZATION OF INTRINSIC STRESSES OF PECVD SILICON NITRIDE FILMS DEPOSITED IN A HOT-WALL REACTOR. Journal de Physique Colloques, 1989, 50 (C5), pp.C5-323-C5-331. 10.1051/jphyscol:1989539 . jpa-00229562

HAL Id: jpa-00229562

<https://hal.science/jpa-00229562>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

CHARACTERIZATION OF INTRINSIC STRESSES OF PECVD SILICON NITRIDE FILMS
DEPOSITED IN A HOT-WALL REACTOR

K. AITE, R. KOEKOEK*, J. HOLLEMAN and J. MIDDELHOEK

University of Twente, ICE Lab., PO Box 217, NL-7500 AE Enschede, The Netherlands

**Tempress BV., Marconistraat 14, NL-7903 AG Hoogeveen, The Netherlands*

Résumé Les contraintes intrinsèques dans les films de Si₃N₄ obtenus par CVD assistée par plasma peuvent entraîner des ruptures durant l'élaboration et durant l'utilisation. L'influence des paramètres de dépôt a été étudiée en insistant sur celle de paramètres peu ou jamais signalés dans la littérature.

Le nitrure de silicium a été déposé sur des substrats de silicium à partir de SiH₄/NH₃ avec ou sans H₂ dans un four à parois chaudes avec un système multi-électrode (température : 350°C, fréquence 50 kHz).

Les contraintes intrinsèques (σ_i) décroissent exponentiellement avec la pression totale (P) suivant la relation $\sigma_i = 24.7 \exp(-1.265P)$. Elles augmentent linéairement avec l'introduction d'azote dans le mélange gazeux et dépendent du rapport SiH₄/NH₃.

L'accroissement de la distance inter-électrodes provoque leur décroissance. Il n'y a pas de corrélation entre les contraintes et la teneur en hydrogène des films de nitrure de silicium.

Les contraintes mécaniques ont été déterminées par la technique des franges de Newton et profilométrie. L'épaisseur du film a été mesurée par ellipsométrie à 632.8nm. La spectroscopie IR(FT) a été utilisée pour déterminer la teneur en hydrogène des films.

ABSTRACT

Intrinsic stresses in PECVD silicon nitride films can cause failure to occur both during device processing and in service. The relevant deposition parameters influencing the intrinsic stresses of the plasma deposited silicon nitride films have been investigated. Emphasis is given to the parameters which were superficially or never reported in the literature.

The silicon nitride films were deposited on 4-inch silicon substrates from SiH₄ and NH₃ with or without N₂ in a horizontal hot-wall reactor with a multielectrode system. The temperature of deposition was typically 350 °C and the rf frequency 50 kHz.

It is shown that the intrinsic stresses (σ_i) of plasma silicon nitride films decrease exponentially with the total gas pressure (P) of the glow discharge, following the relation : $\sigma_i = 24.7 \exp(-1.265 \cdot P)$. The intrinsic stresses of the PECVD silicon nitride films increase linearly with the nitrogen incorporation into the gas mixture and depend on the SiH₄/NH₃ gas ratio. With increasing the interelectrode distance, the intrinsic stresses of the plasma nitride layers decrease. It is further shown that there is no correlation between the intrinsic stresses and the hydrogen content of the plasma silicon nitride films.

The mechanical stresses in the films were determined by the Newton's fringes technique and a surface profiler. The film thickness was measured by ellipsometry at a wavelength of 632.8 nm. FTIR spectroscopy was used to measure the hydrogen content of the plasma nitride films.

INTRODUCTION

Silicon nitride films deposited by Plasma Enhanced Chemical Vapour Deposition (PECVD) are widely used in the field of integrated circuits for passivation because of their impermeability to mobile ions, their hardness (scratch resistance) and the low processing temperature which allows deposition after aluminum metallization [1]. Under certain conditions, large tensile stresses are induced in the deposited films and cracking becomes a serious problem in particular applications where thick films are required. Thus, mechanical stability of PECVD silicon nitride films is an essential property. A strong compressive stress results in voids and cracks in the aluminum lines.

It is well known that the internal stresses of PECVD silicon nitride films are related to the discharge frequency [2-3], and are generally compressive or tensile when deposited at low or high frequencies, respectively. The mechanical properties of thin films can be altered by the implantation or incorporation of impurities during or after growth [4,5,6].

This work shows the influence of the total pressure, gas phase composition, and interelectrode spacing on the intrinsic stress of plasma silicon nitride films deposited in a hot-wall reactor. The relationship between the hydrogen content of the films and their intrinsic stress is also examined.

EXPERIMENTAL

The deposition experiments were performed in a horizontal TEMPRESS hot-wall reactor with a multielectrode system. The deposition system consists of a reactor chamber, a removable wafer boat, a furnace, an rf generator, gas controllers, and a pumping sub-system. The electrodes system was matched to the power supply by an inductive transformer. The whole system was controlled by a programmable digital process controller. The reaction chamber is made of quartz tube and heated by an external three-zones furnace.

Silicon nitride films were deposited from silane (SiH_4) and ammonia (NH_3) with or without nitrogen (N_2). The substrate temperature was set to 350 °C. The rf power was 50 watts and the rf frequency 50 kHz. P-type <100> oriented Si wafers 100 mm in diameter and 25-60 ohm.cm resistivity were used. FTIR studies were performed with silicon nitride films having a minimum thickness of 500 nm, deposited on bare silicon substrates. Background absorption of the substrate was subtracted from the spectra to obtain the bulk film spectra. High resistivity silicon substrates polished on both sides were used in order to prevent dopant absorption and reduce scattering of IR radiation, respectively.

A silicon nitride (Si_3N_4 , which will be written as SiN) film deposited on a silicon substrate is in a state of stress that can be tensile or compressive. Such stresses σ_{SiN} are generally consisting of two components, the thermal stress σ_{th} and the intrinsic stress σ_i :

$$\sigma_{\text{SiN}} = \sigma_{\text{th}} + \sigma_i \quad (1)$$

The thermal stress σ_{th} results from a difference between the thermal expansion coefficient of the film, α_{SiN} , and that of the substrate, α_{Si} . Quantitatively,

σ_{th} is given by :

$$\sigma_{\text{th}} = \frac{E_{\text{SiN}}}{1 - \nu_{\text{SiN}}} \int_{T_{\text{dep}}}^{T_{\text{meas}}} (\alpha_{\text{SiN}} - \alpha_{\text{Si}}) dT \quad (2)$$

and usually approximated by :

$$\sigma_{\text{th}} = \frac{E_{\text{SiN}}}{1 - \nu_{\text{SiN}}} (\alpha_{\text{Si}} - \alpha_{\text{SiN}}) (T_{\text{dep}} - T_{\text{meas}}) \quad (3)$$

This approximation is based on the assumption that α_{Si} , α_{SiN} and the elastic stiffness $E_{\text{SiN}}/(1-\nu_{\text{SiN}})$ of silicon nitride are constant in the range of temperatures used in our experiments (25 - 350 °C).

E_{SiN} and ν_{SiN} are the Young's modulus and the Poisson's ratio of the film, respectively; α_{Si} and α_{SiN} are expansion coefficients for the Si substrate and the silicon nitride film, respectively. T_{dep} is the temperature at which the deposition takes place and the stress measurement is done at T_{meas} . For the film constants we used the values reported by Retajczyk and Sinha [7]: $\alpha_{\text{SiN}} = 1.5 \cdot 10^{-6}/^\circ\text{C}$, and $E_{\text{SiN}}/(1-\nu_{\text{SiN}}) = 1.1 \cdot 10^{11}$ Pa. For Si we have taken $\alpha_{\text{Si}} = 2.6 \cdot 10^{-6}/^\circ\text{C}$ [8]. The total stress in the layers was determined at room temperature by measuring the radius of curvature of the wafers before (R_{bef}) and after (R_{aft}) film deposition with the Newton's rings technique and profilometry (Sloan "Dektak"). Both techniques lead to comparable results within the experimental error. The following equation allows calculation of the average film stress [9]:

$$\sigma_{\text{SiN}} = \pm \frac{E_{\text{Si}}}{6(1-\nu_{\text{Si}})} \cdot \frac{t_{\text{Si}}^2}{t_{\text{SiN}}} \left[\frac{1}{R_{\text{aft}}} - \frac{1}{R_{\text{bef}}} \right] \quad (4)$$

The sign + and - stands for tensile and compressive stresses, respectively. Where t_{Si} and t_{SiN} are the thicknesses of the substrate and the film, respectively. E_{Si} and ν_{Si} are the Young's modulus and the Poisson's ratio of

the substrate, respectively. For Si <100>, the value of $E_{Si}/(1-\nu_{Si})$ is $1.8 \cdot 10^{11}$ Pa. Finally the intrinsic stress component is deduced from eqs.(1), (3) and (4). Films with a minimum thickness of 500 nm were used for the measurements. The stress in the deposited films was independent of the thickness. The flatness of the wafers was better than 2 μm .

RESULTS AND DISCUSSION

As shown in figure 1, the intrinsic stress of near-stoichiometric plasma deposited silicon nitride films decreases with the total gas pressure. The films were deposited from a $\text{SiH}_4\text{-NH}_3$ gas mixture. The stress of the films was always compressive. The plotted data fit the following expression :

$$\sigma_i = 24.7 \exp(-1.265 \cdot P) \quad (5)$$

with a correlation factor $R = 0.99$, σ_i as the intrinsic stress (Pa) and P the total pressure (Torr). This trend is in agreement with results found by other authors [2,10].

Excitation, dissociation and ionization result from inelastic collisions between highly energetic electrons and neutral gas molecules in a glow discharge. The mobility of electrons is higher than that of the ions, therefore the electrode surface charges up to a negative value V_g with respect to the plasma potential [11,12]. A so-called ion sheath region or dark space exists between the glow region, where the potential V_p is almost uniform, and the electrode surface. The ions can follow the low frequency alternating electric field [13], thus those diffusing to the sheath edge are accelerated to the electrode surface with a maximum energy of $(V_p - V_g)eV$. At low pressures ($P < 800$ mTorr), this ion bombardment of the growing film surface becomes very intense, leading to more compressive stress. At high pressures ($P > 1.6$ Torr), the intrinsic stress of the films tends to be independent of the total pressure. In fact, the probability of homogeneous reactions (gas phase) is high in such conditions. Moreover, inelastic collisions in the ion sheath tend to reduce the average ion energy [13]. Figure 2 shows the intrinsic stress versus total pressure for N-rich and Si-rich silicon nitride films deposited from a $\text{SiH}_4\text{-NH}_3$ gas mixture. For both cases the intrinsic stress decreases exponentially with the total pressure as is the case for the near-stoichiometric silicon nitride (Fig. 1). The plotted data fit the following expressions for N- and Si-rich films, respectively :

$$\sigma_i = 23.8 \exp(-1.211 \cdot P) \quad (6)$$

and

$$\sigma_i = 17.26 \exp(-1.095 \cdot P) \quad (7)$$

with a correlation factor $R = 0.99$ for both cases.

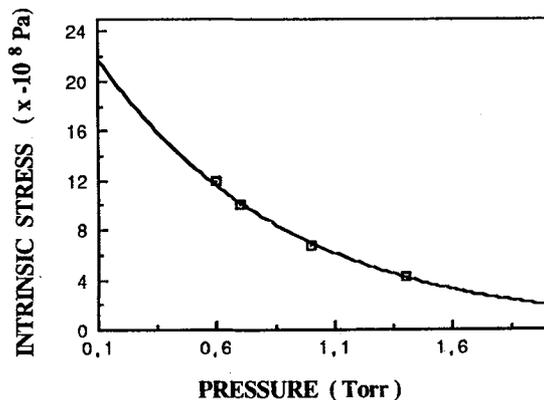


Figure 1. Intrinsic stresses of the PECVD silicon nitride layers vs. total pressure.

Deposition conditions : $\text{NH}_3/\text{SiH}_4 = 7$, rf power = 50 W, rf frequency = 50 kHz, $T = 350^\circ\text{C}$.

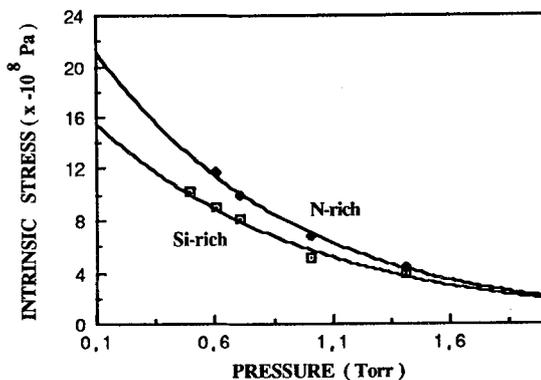


Figure 2. Intrinsic stresses of N-rich and Si-rich PECVD silicon nitride layers vs. total pressure.

Deposition conditions : $\text{NH}_3/\text{SiH}_4 = 5$ for Si-rich films, $\text{NH}_3/\text{SiH}_4 = 15$ for N-rich films, rf power = 50 W, rf frequency = 50 kHz, $T = 350^\circ\text{C}$.

At low pressures ($P < 800$ mTorr), N-rich silicon nitride are more compressive than Si-rich films. The width of the energy spectrum ΔE is inversely proportional to the square root of the ionic mass ($m^{1/2}$), if collisions can be neglected at low pressure conditions [11]. Si-rich and N-rich films were deposited using $NH_3/SiH_4=5$ and $NH_3/SiH_4=15$ gas ratios, respectively. Therefore, more ammonia ionic species which are lighter than silane ionic species, will be present in the discharge of N-rich films deposition. Thus the width of the ion energy spectrum is larger in the latter case and the growing film surface is submitted to a more effective ion bombardment than the Si-rich films.

A linear relationship was found between the intrinsic stress and the partial pressure of nitrogen for films deposited from a $SiH_4-NH_3-N_2$ gas mixture (Fig.3). The nitrogen concentration was changed by varying the ratio of the input gases N_2 and NH_3 while the (N_2+NH_3) and SiH_4 flows were kept constant at 550 and 50 sccm, respectively. The number of N_2^+ ions increased with the nitrogen partial pressure [6] and the ion bombardment of the growing film surface was enhanced. Implanted ions caused an expansion of the film parallel to the surface. Therefore the film became under more compressive stress.

The intrinsic stress of the plasma deposited silicon nitride films decreases with increasing the interelectrode distance as shown in figure 4. Increasing the interelectrode distance also means decreasing the probability of ions reaching the growing film surface. Therefore, the ion bombardment of the film surface is decreased. The homogeneous reaction probability also increases with the interelectrode spacing, leading to lower density films. For small interelectrode distance values, the ion bombardment is very intense, resulting in a very high compressive stress. Interelectrode spacing smaller than 15 mm resulted in sparks and extinction of the discharge.

Figure 5 shows that there is no correlation between the intrinsic stresses and the hydrogen content of the plasma silicon nitride films. A presence of molecular hydrogen in PECVD a-Si:H films was reported by Chabal et al [15]. The presence of such molecular hydrogen has a substantial effect on the stress of silicon nitride films [16]. Silicon nitride films with comparable amount of bonded hydrogen can have different values of intrinsic stress (fig.5). Therefore, the intrinsic stress of plasma deposited silicon nitride films cannot be related to their bonded hydrogen.

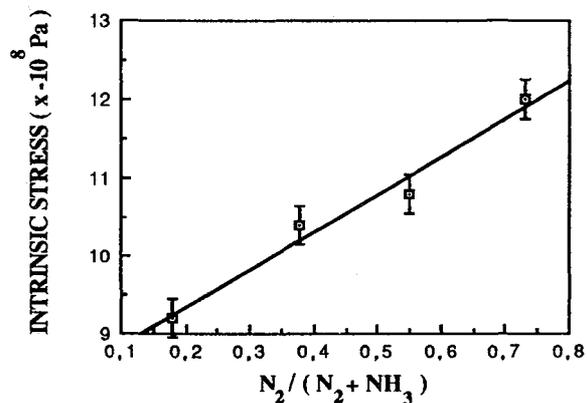


Figure 3. Intrinsic stresses of the PECVD silicon nitride layers vs. gas flow ratio $N_2/(N_2+NH_3)$.

Deposition conditions : $(N_2+NH_3) = 550$ sccm, $SiH_4 = 50$ sccm, rf power = 50 W, rf frequency = 50 kHz, total pressure = 100 Pa, $T = 350^\circ C$.

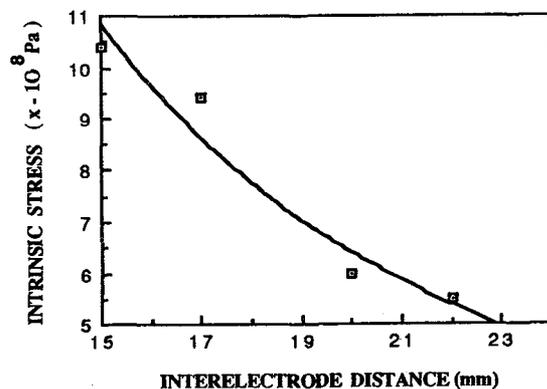


Figure 4. Intrinsic stresses of the PECVD silicon nitride layers vs. interelectrode distance.

Deposition conditions : $NH_3/SiH_4 = 7$, rf power = 50 W, rf frequency = 50 kHz, $T = 350^\circ C$.

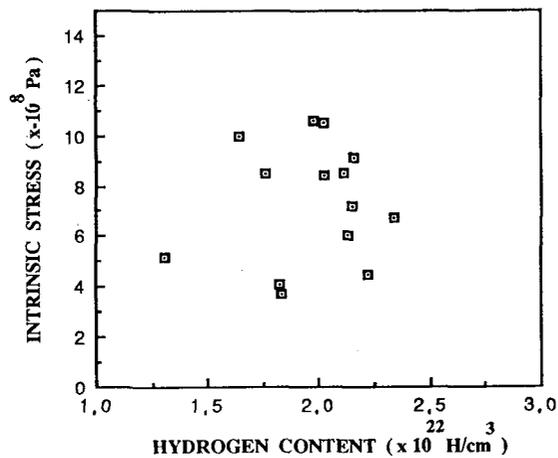


Figure 5. Intrinsic stress vs. hydrogen content in the PECVD silicon nitride films.

CONCLUSION

The intrinsic stresses of plasma silicon nitride films decrease exponentially with the total gas pressure. At low pressures, an intense ion bombardment of the growing film surface leads to higher compressive stresses in the deposited layers. The intrinsic stresses of the PECVD silicon nitride films increase linearly with the nitrogen incorporation into the $\text{NH}_3\text{-SiH}_4$ gas mixture. N-rich plasma silicon nitride films deposited at low pressures, show higher compressive stresses relative to Si-rich layers. Finally, there is no correlation between the intrinsic stresses and the bonded hydrogen of plasma deposited silicon nitride films.

REFERENCES

- [1] J.R. Hollahan and R.S. Rosler, in "Thin Film Processes", edited by J.L. Vossen and W. Kern, Academic Press, N.Y., p. 335, (1978).
- [2] W.A.P. Claassen, W.G.J.N. Valkenburg, M.F.C. Willemsen, and W.M.v.d. Wijgert, J. Electrochem. Soc., **132**, p. 893, April 1985.
- [3] A.K. Sinha, H.J. Levinstein, T.E. Smith, G. Quintana, S.E. Haszako, J. Electrochem. Soc., **125**, pp. 601-8, (1978).

- [4] Thornton J.A., In Deposition Technologies for Films and Coatings, ed. R.F. Bunshah, pp. 170-243. Park Ridge : Noyes publications, (1982).
- [5] Eernisse E.P., J. Appl. Phys., **48**, 3337-41, (1977).
- [6] K.Aite, J.Holleman, J. Middelhoek and R. Koekoek, Proceedings of the MRS Fall Meeting, **130**, (Boston Massachusetts Nov. 28-30, 1988).
- [7] T.F. Retajczyk, Jr., and A.K. Sinha, Thin Sol. Films, **70**, 241 (1980).
- [8] P.J. Burkhardt and R.F. Marvel, J. Electrochem. Soc., **116**, 864 (1969).
- [9] "Physics of Thin Films", Vol.2, pp.211-273, edited by G.Haas and R.F. Thun, Academic Press, New York (1966).
- [10] D.Illic, Solid State Technol., pp. 91-92, (April 1982).
- [11] J.W. Coburn and E. Kay, J. Appl. Phys., **43**, 4365 (1972).
- [12] J.L. Vossen, J. Electrochem. Soc., **126**, 319 (1979).
- [13] W.D. Davis and Vanderslice T.A., Phys. Rev., **131**, 219, (1963).
- [14] Hirose M., Semiconductors and Semimetals, Vol. 21 A, Pankove J.I., Ed., Academic Press, New York, p.12, (1984).
- [15] Y.J. Chabal and C.K.N. Patel, in Proceedings of the 17th International Conf. on the Phys. of Semicond., ed. by D. Chadi and W.A. Harrison (Springer, New York, 1985), p. 909.
- [16] R.C. Budhani, R.F. Bunshah and P.A. Flinn, Appl. Phys. Lett.,**52**(4), 25 January 1988.