Pulsed laser deposition of non-stoichiometric silicon nitride (SiN_x) thin films

J.M. Lackner[1,2], W. Waldhauser[1], R. Ebner[1,2], M. Beutl[3], G. Jakopic[3], G. Leising[3], H. Hutter[4], M. Rosner[4]

[1] JOANNEUM RESEARCH, Laser Centre Leoben, Leobner-Strasse 94, A-8712 Niklasdorf, Austria
[2] Materials Center Leoben, Franz-Josef-Strasse 13, A-8700 Leoben, Austria
[3] JOANNEUM RESEARCH, Institute of Nanostructured Materials and Photonics, Franz-Pichler-Strasse 30, A-8160 Weiz, Austria
[4] Institute of Chemical Technology and Analytics, Vienna University of Technology, Getreidemarkt 9, A-1060 Wien, Austria

Abstract

Silicon nitride (SiN_x) thin films of various stoichiometries (x) were prepared on Si (100) substrates applying the Nd:YAG (λ = 1064 nm) pulsed laser deposition (PLD) process in the "shaded off-axis" technique at room temperature. The specific arrangement of this technique with perpendicular target (Si) and substrate surfaces and a metallic screen in between guarantees very low particulate (droplet) deposition and, thus, excellent surface qualities. Compared to the usually used "on-axis" deposition technique consisting of a parallel arrangement of the target and substrate surface, the coating surface covered with particulates is about 100 times lower reaching a maximum of 0.2 % on 400 nm thick films. The variation the N_2 partial pressure affects the nitrogen content and the silicon bonding structure of the films analysed by means of SIMS and XPS, respectively. As a consequence the optical properties (e.g. refractive index) are tailorable in a wide spectral range between 250 and 1200 nm.

PACS: 81.15 Fg, 78.20 Ci

1. Introduction:

Silicon nitride (Si_3N_4) is one of the most interesting thin film materials in the semiconductor and optoelectronic device technology [1,2]. The outstanding advantage of thin films in the silicon – nitrogen system are the tailorable electronical and optical properties, which are highly dependent on the chemical composition. Thus, the deposition of non-stoichiometric silicon nitride (SiN_x, $x \neq 4/3$) desires a precise manipulation of the manufacturing parameters. Furthermore, low temperatures are requested to prevent damage of the devices during film deposition. One of the most suitable techniques combining room temperature deposition with precise manipulation of the deposition parameters is the Pulsed Laser Deposition (PLD) [3-8]. This technique is based on a pulsed laser beam evaporating the target material and ionizating the vapour. Besides the ablation of vapourized material also solid and liquid material is ejected from the target, which leads to inadequate surface qualities of the grown films. To overcome this major problem various proposals have been discussed in the past (e.g. in [9]). One approach is the "shaded off-axis" technique [10,11], applying a perpendicular arrangement of the target and substrate surfaces combined with a metallic screen to protect the substrate against direct particle flow. The aim of the present work was the application of this technique to the PLD of SiN_x thin films from silicon substrates in nitrogen-containing atmospheres.

J.M. Lackner: Tel. ++43 3842 81260 2305, Fax. ++43 3842 81260 2310, Email. juergen.lackner@joanneum.at
W. Waldhauser: Tel. ++43 3842 81260 2311, Fax. ++43 3842 81260 2310, Email. wolfgang.waldhauser@joanneum.at
R. Ebner: Tel. ++43 3842 45922 4, Fax. ++43 3842 45922 5, Email. ebner-r@mcl.at
M Beutl : Tel. ++43 316 876 2723, Fax. ++43 316 8769 2723, Email. michael.beutl@joanneum.at
G. Jakopic : Tel. ++43 316 876 2703, Fax. ++43 316 8769 2703, Email. georg.jakopic@joanneum.at
G. Leising : Tel. ++43 316 876 2701, Fax. ++43 316 8769 2701, Email. guenter.leising@joanneum.at
H. Hutter : Tel. ++43 1 58801 15120, Fax. ++43 1 58801 15100, Email. hhutter@pop.tuwien.ac.at
M. Rosner : Tel. ++43 1 58801 15120, Fax. ++43 1 58801 15100, Email. hhutter@pop.tuwien.ac.at

2. Experimental

2.1 Film deposition

High purity silicon targets (99.95 % Si) were used for the ablation experiments using a pulsed Nd:YAG laser, which provides a beam with 1064 nm wavelength, 0.85 J pulse energy and 10 ns pulse duration at a repetition rate of 10 Hz. The targets were rotated during the laser irradiation in order to avoid the formation of deep craters. The emitted species were deposited at room temperature (~ 25 °C) onto single crystalline (1 0 0) orientated silicon substrates mounted normal to the target behind a screen of 1 cm heigth ("shaded off-axis" technique), for details see [11]. By using this technique the coating surface covered with particulates is about 100 times lower reaching a maximum of 0.2 % on 400 nm thick films compared to the usually used "on-axis" deposition technique consisting of a parallel arrangement of the target and substrate surface. Prior to deposition the substrates were cleaned ultrasonically in pure acetone and ethanol to remove surface contaminations. The reaction chamber was evacuated before starting the deposition process to pressures below $2x10^{-3}$ Pa by a pumping unit consisting of a rotating and an oil diffusion pump. The flows of the process gases (Ar, N_2) (Table 1), which are necessary for the scattering the ablated species behind the screen to reach the substrate surface, were adjusted by means of electronic mass flow controllers.

2.2 Film characterization

X-ray diffraction (XRD) (Bruker AXS D8 Discover) in grazing angle alignment (0.5° and 1.0°) with CuKα radiation was used for determining the crystal structure of the thin films. The charactization of the chemical film composition occurred by secondary ion mass spectroscopy (SIMS) using a CAMECA IMS 3f [12]. The system has approximately 2 µm lateral and 20 nm vertical resolution. A stoichiometric Si_3N_4 (direct nitrided and hot pressed Si_3N_4 powder) was taken as the standard material for the quantitative analysis.

The determination of the chemical bonding occurred by X-ray photoelectron spectroscopy (XPS) using an Omicron Multiprobe system with a monchromized AlKα (1486.6 eV) X-ray beam and a resolution of the analyzer better than 0.3 eV [13]. The detection sensitivity was approximately 1 mass%.

The optical properties of the films were determined using a variable angle spectroscopic ellipsometer (J.W. Woollam Comp. Inc.) at angles of incidence between 65 and 85° in the spectral range from 360 to 900 nm with 2 nm spectral resolution. For calculating the refractive indices of the silicon rich films the Cauchy dispersion [14] was applied. In contrast, the fitting of the refractive indices of the nitrogen rich films was performed using a graded interface two component model [15] consisting of stoichiometric silicon nitirde (Si_3N_4) [16] as top layer and Si-rich silicon nitride [17] as base layer.

3. Results and discussion

3.1 Structural and morphological characterization

The XRD investigations using grazing incidence alignment indicate the fully amorphous structure of all nearly particulate free and very smooth films (Film: R_a ~ 1.0 nm, Si substrate: R_a ~ 1.8 nm). Similar results were found in TEM investigations of PLD silicon and silicon oxide thin films [11] and can be attributed to the low energy of the deposited atoms on the sample surfaces during film growth. Although the vaporized target material is partly ionized during the laser ablation, the low energies of the deposited species are characteristic for the PLD in the "shaded off-axis" arrangement [10,11], which requires a scattering of the ablated species for reaching the substrate surface. Thus, the surface as well as the bulk diffusion processes, which are necessary for crystal growth in the films, cannot be activated by the low energies during deposition at the low substrate temperatures (~ 25 °C).

3.2 Chemical characterization

SIMS measurements were used to determine the chemical composition of the films. The depth profiles, shown for the film S1 and S4 deposited in Ar and N_2 atmosphere, resp., in Fig. 1, indicate low contents of contaminations like oxygen, carbon and hydrogen in the grown films. Furthermore, an increase of their concentrations near the native oxide layer covering the silicon wafer can be observed. Comparing the element count rates of O and H of the N-rich film S4 (Fig. 1b) and the nearly N-free film S1 (Fig. 1a), about 10 times lower O and a little higher H contaminations are present in the latter film, which can be attributed to differences in the purity of the gases (Ar, N_2) used. The count rate for the nitrogen containing species detected (SiN, CN) in all films deposited in N_2 containing atmospheres (e.g. S4 in Fig. 1b) is nearly constant over the whole film thickness. The quantitative N contents in the films calculated using a stoichiometric Si_3N_4 standard are shown in Table 1, indicating an increase of the nitrogen content at higher N_2 gas flows during deposition.

This increase of the nitrogen content was also found in the XPS investigations of the silicon peaks. The bonding energy of the silicon atoms is shifted from 99.2 eV in the film S1, which is the characteristic value for the metallic bonding (Si^0) of the Si atoms [18,19], to 100.9 eV and 101.5 eV for the films S2 and S3, resp.. The bonding energy of 100.9 eV can be attributed to the chemical bonding of a central Si atom with two Si and two N atoms in its surrounding [20], resulting in a Si^{2+} or Si_3N_2 structure. Small contents of Si_3N_4 type bonding (Si^{4+}) are indicated by the non-symmetrical shape of the Si XPS peaks. Fully Si_3N_4 type bonding, characterized by the Si^{4+} state (binding energy ~ 103.2 eV) and, thus, only Si-N bonds [19,20], dominates the chemical structure of the N rich film S4. For the N atoms binding energies of about 397.5 eV are found for all films deposited in reactive N_2 atmosphere, indicating the N^{3-} state of the N atoms and, thus, 3 saturated bonding sites for Si atoms [21].

Slight shifts of these binding energies are caused by electrostatic charging during the XPS measurements.

3.3 Optical characterization

The differences in the chemical composition and bonding crucially influence the optical behaviour of the films. The dependencies of the refractive indices on the wavelengthes between 260 and 900 nm are shown in Fig. 2. For the nearly pure Si thin film S1 the optical behaviour can be described excellently by amorphous Si (a-Si) [16]. For the films with high N contents (S3, S4) the optical constants fit well with data of non-crystalline, stoichiometric Si_3N_4 [16]. The optical behaviour of the film S2 represents a transition between a-Si and Si_3N_4, like the Si-rich Si_3N_4 labeled functions [17].

These results verify the varying bonding structure of the Si atoms in amorphous Si-N networks found in the XPS investigations. Si-Si bonds are replaced by Si-N bonds at higher N contents of the films. Reasonably, the bonding of the Si atoms changes from the metallic Si^0 structure to Si^+, Si^{2+} and Si^{3+} at higher N concentrations and finally, reaching the saturation of the four possible bonding sites of the Si atoms by four N atoms, to Si^{4+}. The N atoms possess independently on the N content in the films S2, S3 and S4 deposited in N_2 atmosphere three binding sites (N^{3-} structure), which are all bonded to Si atoms in their surrounding. These results confirm a network of Si and N atoms with lower order only on the atomic scale described by Karcher et al. [20] for non-stoichiometric SiN_x ($x \neq 4/3$) films.

4. Conclusions

The Pulsed Laser Deposition (PLD) technique with a Nd:YAG laser (1064 nm wavelength) was applied for manufactoring thin films in the silicon-nitrogen system from silicon targets at room temperature. The application of the shaded off-axis PLD technique with a perpendicular arrangement of the target and the substrate surfaces and a screen in between for preventing a direct deposition without scattering lead to nearly particulate (droplet) free films with very smooth surfaces and dense structures. The necessity of scattering decreased the energy of the vapourized atoms and clusters deposited and, thus, lead to fully amorphous film structures. These collisions between the Si atoms and N_2 molecules cause chemical reactions, which are mainly responsible for the chemical composition of the films, found between nearly pure Si for the deposition in Ar atmosphere and Si_3N_4 in N_2 containing atmospheres. The optical behaviour (refractive indices) of these films is compareable with amorphous silicon and stoichiometric Si_3N_4 found in literature, whereas the film with a lack of nitrogen shows a transition-like behaviour between these two compounds. This phenomenon confirms the Si-N bonding structure in the amorphous films changing between Si^0, S^{i+}, Si^{2+}, Si^{3+} and Si^{4+} with increasing N content found in the XPS investigations. In contrast, the nitrogen atoms are independently to the N_2 flow used for deposition N^{3-} bonded with Si atoms in their surrounding.

5. Acknowledgements:

Financial support of this work by the Austrian Federal Ministry of Traffic, Innovation and Technology, the Government of Styria, the Technologie Impulse Gesellschaft mbH in the frame of the Kplus Programme and the European Union is highly acknowledged. The authors are grateful to R. Berghauser (Laser Center Leoben) for assisting the film deposition.

References:

[1] A. Ouacha, M. Willander, B. Hammarlund, R.A. Logan: J. Appl. Phys. **74**, 5602 (1993)

[2] L. Shi, A.M. Steenberger, A.H. de Vreede: J. Vac. Sci. Technol. **A14**, 471 (1996)

[3] E.C. Samano, R. Machorro, G. Soto: Appl. Surf. Sci. **127-129**, 1005 (1998)

[4] E. d'Anna, G. Leggieri, A. Luches: Appl. Surf. Sci. **86**, 170 (1995)

[5] V.S. Teodorescu, L.C. Nistor, M. Popescu: Thin Solid Films **397**, 12 (2001)

[6] Y. Suda, K. Ebihara, K. Baba: NanoStructured Materials **12**, 391 (1999)

[7] W.-J. Wu, M.-H. Hon: Thin Solid Films **345**, 200 (1999)

[8] I. Umezu, T. Yamaguchi, K. Kohno: Appl. Surf. Sci. **197-198**, 376 (2002)

[9] D.B. Chrisey, G.K. Hubler (Eds.): Pulsed Laser Deposition of Thin Films (John Wiley & Sons, New York 1994)

[10] E. Agostinelli, S. Kaciulis, M. Vittori-Antisari: Appl. Surf. Sci. **156**, 143 (2000)

[11] J.M. Lackner, W. Waldhauser, R. Ebner, W. Lenz, C. Suess, G. Jakopic, G. Leising, H. Hutter: Surf. Coat. Techn. **163-164**, 300 (2003)

[12] K. Piplits, W. Tomischko, C. Brunner, H. Hutter: Proceedings of the 10th International Conference on Sec. Mass Spectr. SIMS **10**, 1007 (1997)

[13] EA 125 Energy Analyser User's Guide, Version 2.0 (Omicron GmbH, Traunusstein, Germany, 2001)

[14] O. Stenzel: Das Dünnschichtspektrum (Akademie-Verlag, Berlin 1996)

[15] D.-E. Aspnes: Amer. Journ. Phys. **50**, 704 (1982)

[16] E.D. Palik: Handbook of Optical Constants of Solids (Academic Press, Orlando (FL) 1990)

[17] Data bank of ellipsometer software WVASE32 (J.A. Woollam Co. Inc., Lincoln (NE) 2000)

[18] E. Dehan, P. Temple-Boyer, R. Henda: Thin Solid Films **266**, 14 (1995)

[19] I. Bertoti I.: Surf. Coat. Techn. **151-152**, 194 (2002)

[20] R. Karcher, L. Ley, R.L. Johnson: Phys. Rev. **B30**, 1896 (1984)

[21] T. Aiyama, T. Fukunaga, K. Niihara: J. Non-Cryst. Solids **33**, 131 (1979)

Figures and Tables:

Fig. 1: SIMS depth profiles of the PLD films (a) S1 and (b) S4, deposited in atmospheres of 30 sccm Ar and 60 sccm N_2, resp.). The measured counts of SiN and CN ions and O, H and C contaminations are related to 10^5 counts of Si ions.

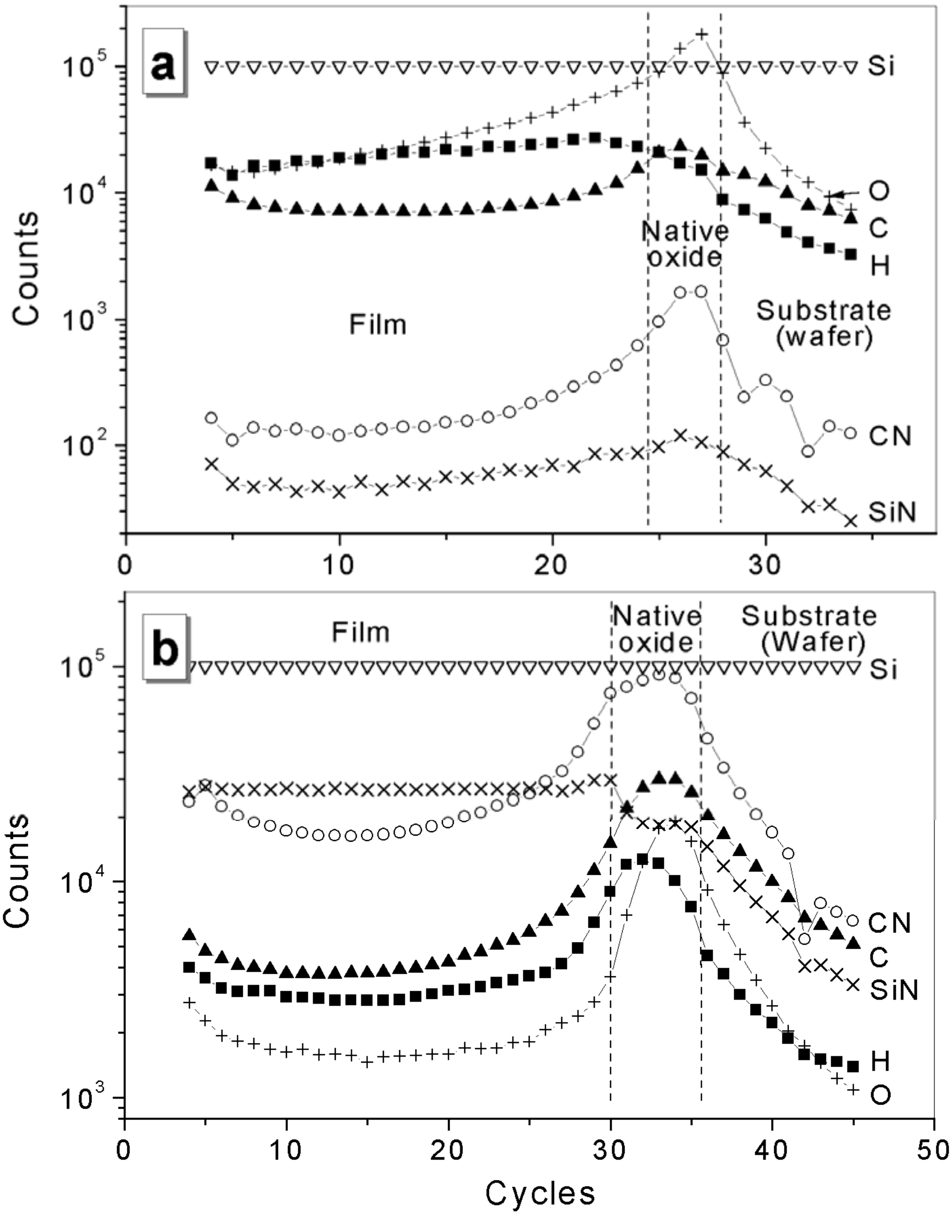
Fig. 2: Dependency of the refractive indices of the PLD thin films on the light wavelength characterized by spectroscopic ellipsometry. Besides the optical behaviour of the films deposited the functions of amorphous Si (a-Si) [16], stoichiometric Si_3N_4 [16] and Si-rich silicon nitride [17] are shown.

Table 1: Deposition parameters, chemical compositions and binding energies of the Si atoms of all PLD thin films deposited

Table 1:

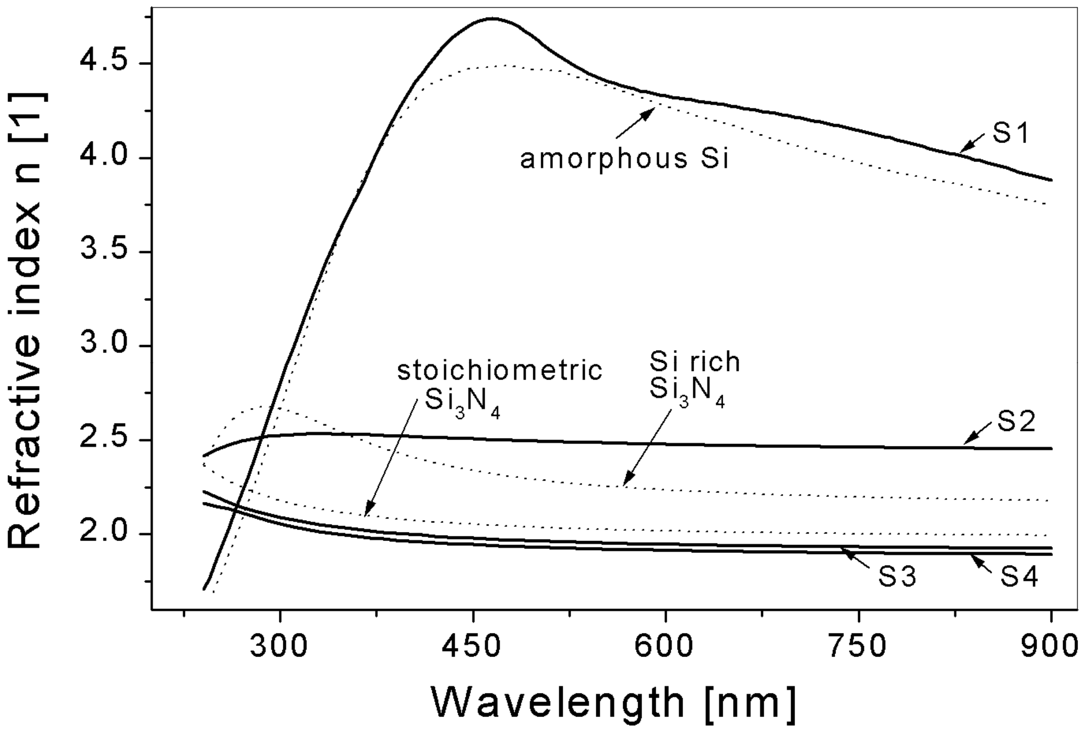
Film / Sample	Process gas flow [sccm]		Ambient pressure [Pa]	Nitrogen content [%]	Binding energy of Si [eV]
	Ar	N_2			
S1	30	0	1.8	0.09	99.2
S2	25	5	1.8	44.0	100.9
S3	0	30	1.7	47.5	101.5
S4	0	60	2.1	54.5	103.2

Fig. 1:



a
Si
O
C
H
Native oxide
Film
Substrate (wafer)
CN
SiN
Counts
b
Film
Native oxide
Substrate (Wafer)
Si
CN
C
SiN
H
O
Counts
Cycles

Fig. 2:



Refractive index n [1]
4.5
4.0
3.5
3.0
2.5
2.0
300
450
600
750
900
Wavelength [nm]
amorphous Si
S1
stoichiometric
Si3N4
Si rich
Si3N4
S2
S3
S4